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IX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

By Henry B. Hill.

Presented June 9, 1880.

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In December, 1876, by the kind invitation of Dr. E. R. Squibb, I had the opportunity to examine the working of a new process for the manufacture of acetic acid by the dry distillation of wood at a low and carefully regulated temperature, as it was carried on under his direction at Brooklyn, N. Y. I then noticed that, in the rectification of the crude wood spirit, a yellowish oil passed over with the vapor of water after the more volatile portions had been distilled off. Its high specific gravity and its peculiar odor made me anxious to examine it more closely.

A short study of it was sufficient to show that it contained large quantities of furfurol which could be isolated in a pure state with little trouble, and I therefore undertook at once the study of the constitution of furfurol and pyromucic acid. Before my investigations were far advanced, Baeyer * published the first of his papers upon the constitution of furfurol, in consequence of which my own work was naturally discontinued. At the same time, however, I wrote to Professor Baeyer asking if I could not make use of the large supply of material which I had at hand without interfering with the plan of his research. In reply I received the extremely considerate intimation that a study of mucobromic acid and its derivatives would in no way interfere with his work.

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* Berichte der deutsch. chem. Gesellsch., x. 355.

This investigation was begun in 1877; and, although it is not yet completed, so many facts have accumulated that I have thought it best to lay before the Academy the results already obtained.

Different portions of this research I have carried on with Mr. O. R. Jackson and Mr. C. F. Mabery, assistants in this laboratory, and with Mr. W. Z. Bennett. In my description of our results, I shall make plain the share which each of these gentlemen has had in the work.

My most sincere thanks are due to Dr. Squibb for the generous supply of material, without which it would have been impossible for me to have undertaken this investigation.

FURFUROL ONE OF THE PRODUCTS OF THE DRY DISTILLATION OF WOOD.

Although the products formed in the dry distillation of wood have repeatedly been made the subject of investigation, I can find in the literature of the subject but little reference to the presence of furfurol among them. That furfurol is thus formed is asserted by Gmelin [*] on the authority of Völkel, but a close examination of Völkel's original papers [†] fails to show any sufficient foundation for the assertion. Although Völkel had already shown that furfurol was formed in the dry distillation of sugar, and had established its presence by analysis,[‡] in his subsequent work upon the dry distillation of wood he seems to have based his conclusions solely upon qualitative tests by no means conclusive. Although he makes a number of general statements concerning the presence of furfurol among the products he obtained, I can find nothing more definite than is contained in the following passage.[§]

After describing the extraction of a yellowish brown oil from the pyroligneous acid by means of ether he proceeds: "In Kalilauge löst sich das Oel unter Entwicklung eines betäubenden Geruchs auf, der von einer geringen Menge einer organischen Basis herrührt, weil er auf Zusatz von Säure wieder verschwindet. Die dunkel gefärbte alkalische Lösung trübt sich in kurzer Zeit durch Ausscheiden eines gelbbraunen Körpers, der Pyroxanthin enthält. Aus der abfiltrirten noch stark gefärbten alkalischen Flüssigkeit wird durch verdünnte Schwefelsäure ein anderer brauner Körper abgeschieden, und zugleich der Geruch des Kreosots wahrgenommen. Aus diesen Reactionen ergiebt sich dass das Oel . . . ein sehr gemengtes . . . ist. Es enthält ein eigenthümliches Oel (Pyroxanthogen), das durch die Einwirkung von Alkalien in Pyroxanthin übergeht; Kreosot; ferner mehrere flüchtige Oele, die durch Alkalien in braune Körper umgeändert werden die in Kali theils löslich theils unlöslich sind. Diese letzteren Oele sind unstreitig identisch mit den flüchtigeren Oelen die bei der Destillation des Zuckers erhalten werden, Furfurol, u. s. w." I have quoted the passage with but little abbreviation, that the character of the qualitative tests upon which Völkel based his conclusion may be appreciated.

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[*] Gmelin's Handbuch, vii. 599; Suppl., ii. 972.

[†] Poggendorff's Annalen, lxxxii. 496; lxxxiii. 272 and 557; Ann. Chem. u. Pharm., lxxxvi. 66.

[‡] Ann. Chem. u. Pharm., lxxxv. 59.

[§] Ibid., lxxxvi. 83.

Quite recently since the publication of a preliminary note by me upon this subject, V. Meyer [*] has found in the commercial glacial acetic acid of the continent, a small quantity of furfurol which manifested itself by the intense red color developed when the acid was mixed with aniline.

Although these two observations are all I can find recorded of the presence of furfurol among the products of the dry distillation of wood, its formation from wood by other means has been more frequently noticed. Although Döberciner [†] could obtain no furfurol from sawdust by distillation with sulphuric acid, Fownes [‡] none from linen, and Cahours [§] and Gudkow [¶] were equally unsuccessful with pure cellulose, Emmet [**] obtained it by the same method from woody fibre, Stenhouse [††] from sawdust, afterward from mahogany [‡‡] and madder.[§§] Gr. Williams [¶¶] also found that it was formed when wood was heated under pressure with water, although none could be obtained at ordinary pressures. Similar results were obtained by H. Müller.[***]

A brief description of the method of distillation which has furnished the material for this investigation may prove of interest: since the product obtained in this way contains considerable quantities of furfurol, while the percentage formed by the ordinary methods must be very small to have escaped notice so generally. The wood, chiefly oak, is cut into small pieces and filled into rectangular retorts of boiler iron, each one capable of holding a charge of from five to six thousand kilogrammes. The retorts when charged are placed in separate cells of an oven heated by hot-air flues. The temperature of this oven is carefully regulated by means of long mercurial thermometers built into each cell, and the thermometer readings vary from 150° at the beginning of a distillation to 200° at the end. The average time required is six days, and during this time the wood loses about thirty-two per cent of its weight. The volatile products pass through an outlet pipe at the top of each retort, and are condensed in a set of ordinary coolers.

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[*] Berichte der deutsch. chem. Gesellsch., xi. 1870.

[†] Journ. pract. Chem., xlvi. 168.

[‡] Pharmaceutical Journal and Transactions, viii. 113.

[§] Ann. Chim. Phys., [3] xxiv. 277.

[¶] Zeitschr. für Chem., 1870, 360.

[**] Amn. Jour., xxxii. 140.

[††] Ann. Chem. u. Pharm., xxxv. 301.

[‡‡] Ibid., lxxiv. 278.

[§§] Ibid., lxxx. 325.

[¶¶] Chem. News, xxvi. 231 and 293.

[***] Ibid., xxvi. 247.

The wood left in the retorts after distillation is darker in color and somewhat more brittle than the fresh wood: its composition agrees essentially with that given by Payen* for dried oak wood. The specimens of wood for analysis were taken while still warm from the retorts, and kept hermetically sealed until analyzed.

I. 0.4480 grm. substance gave 0.8950 grm. CO_2, 0.2545 grm. H_2O and 0.0040 grm. ash.

II. 0.3880 grm. substance gave 0.7810 grm. CO_2 and 0.2220 grm. H_2O. 1.2725 grm. of the same wood gave 0.0070 grm. ash.

III. 0.3270 grm. substance gave 0.6390 grm. CO_2, 0.1740 grm. H_2O and 0.0015 grm. ash.

	Found.			Payen.
	I.	II.	III.	
C.	50.01	54.89	53.30	54.44
H.	5.88	6.29	5.78	6.24
Ash.	0.89	0.55	0.46	

The volatile products of the distillation are subjected to the ordinary processes of rectification. In fractioning the wood spirit, after the more volatile portions have passed over, the distillate throws down a heavy yellow oil upon dilution with water, and somewhat later the slightly acid aqueous distillate contains an abundance of the same heavy oil in suspension. The quantity of oil which thus separates in the course of distillation amounts to between three and four tenths of one per cent of the crude wood spirit taken, although I am unable to form even an approximate estimate of what proportion this may be of the total amount present.

The oil, as I received it, was feebly acid to test paper, and had a peculiar aromatic odor. It was bright yellow in color, and slightly heavier than water. It was washed with water dried over calcic chloride and submitted to fractional distillation. The liquid began to boil a little above 100° ; but the thermometer rose rapidly, and had reached 160° before any considerable quantity had passed over ; between 160 –170° it remained stationary for a long time, and then rose again rapidly to over 200°. After several distillations, about sixty per cent of the oil taken distilled between 160° and 165°, the greater part of which boiled steadily at 162°. The boiling point and general character of the oil at once suggested the presence of furfurol, and this was readily proved by its conversion into furfuramide, furfurine, and pyromucic acid. The behavior of the oil to alkalies, however, showed that it was still by no means homogeneous. When shaken with a dilute solution of potassic or sodic hydrate, a brilliant yellow color was developed; and in a few moments the clear liquid became turbid with the separation of a flocculent yellow precipitate, which proved to be chiefly pyroxanthin. In following out the method of purification which was thus suggested, I found it most convenient to separate from the crude oil, only so much of the higher boiling constituents as could be removed by rejecting that which passed over above 175° in two successive distillations. The distillate collected below 175° was then gradually mixed with one-fourth its volume of a concentrated solution of sodic hydrate, taking care to keep the mixture cool, and shaking the two well together. After standing a short time, the oil was separated from the alkaline solution, washed with a little water, and distilled with steam. The furfurol thus obtained was sufficiently pure for all ordinary purposes, and from such a product was made all the pyromucic acid which has been used in the course of the following investigations.

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* N. Ann. Sci. Nat., xi. 24.

For its conversion into pyromucic acid, it was mixed with an equal volume of a concentrated alcoholic solution of sodic hydrate, and carefully stirred until the violent reaction was over. The sodium salt was then thoroughly washed with ether, dissolved in hot water, and decomposed by concentrated hydrochloric acid. For the purification of the crude acid, it was dissolved in a cold dilute solution of sodic carbonate, taking care that the solution should remain slightly acid. The filtered solution of the sodium salt was boiled with bone-black filtered, concentrated by evaporation, and finally acidified with hydrochloric acid. The acid which separated on cooling was then recrystallized from boiling water, and was found on analysis to be sufficiently pure for further use.

0.8140 grm. substance gave 1.5910 grm. CO_2 and 0.2910 grm. H_2O.

	Calculated for $C_5H_4O_3$.	Found.
C	53.57	53.31
H	3.57	3.97

The acid prepared in this way melted at 128–129°; and, since the melting point of pyromucic acid is usually given somewhat higher, it seemed advisable to subject this product to further purification. Mr. J. J. Thomsen, therefore, prepared the ethyl-ether of the acid by saturating its solution in absolute alcohol with hydrochloric acid, precipitating with water, and washing first with a dilute solution of sodic carbonate and then with water. He then found that the carefully dried ether distilled from the first drop to the last unchanged at 195° (Mercury column completely in vapor) under a pressure of 766 mm. On cooling, it crystallized in large transparent prisms, which melted at 34°. According to Malaguti,* ethyl pyromucate melts at 34°, but boils at 208 – 210°, under a pressure of 756 mm. For the determination of boiling point, we employed about 30 grm. of the ether, and an analysis showed its purity.

0.5615 grm. of substance gave 1.2330 grm. CO_2 and 0.2940 grm. H_2O.

	Calculated for $C_5H_3O_3C_2H_5$.	Found.
C	60.00	59.8
H	5.71	5.81

A portion of this ether was saponified with sodic hydrate, the acid liberated from the sodic salt, recrystallized from hot water several times, and finally melted. The solidified acid melted at 130°.5 (uncom.), while an acid made directly from mucic acid melted at 130°. The corrected melting points of the two were 133° and 132.°5; whereas Schwanert† gives the corrected melting points 134°.3 and 132.°6 respectively for substance made from furfurol and from mucic acid. The chief constituent of the oil under investigation was thus shown to be furfurol. From the higher boiling portions, I have as yet been able to isolate no well-marked substances. On distillation, the thermometer rose slowly to over 300°, and even after long fractioning there appeared to be no tendency towards constant boiling points. By far the greater portion was insoluble in alkalies, and I could obtain no characteristic derivatives by the action of various reagents.

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* Ann. Chim. Phys., [2] lxiv. 279.

† Ann. Chem. u. Pharm., cxvi. 257.

From the sodic hydrate used for washing the crude furfurol could be separated in small quantity an oil volatile with steam, and possessing a strong odor like smoked fish. It had the general characters of a phenol, but I have not as yet further identified it. Since a large quantity of material has been accumulated in preparing the furfurol necessary for the following researches, I hope before long to make further study of the less volatile constituents which are present in smaller quantity.

PYROXANTHIN.

I have already mentioned the yellow flocculent precipitate, formed by the action of alkalies upon the crude furfurol, which upon examination proved to consist chiefly of pyroxanthin. This substance was discovered in 1835 by Dr. Scanlan,[*] of Dublin, in the residue from the preparation of methyl alcohol from crude wood spirit by means of lime. In 1836, it was further studied by Apjohn and Gregory,[†] who deduced from their analyses the formula $C_{21}H_{18}O_4$, although they did not succeed in confirming this formula by the preparation and analysis of any of its derivatives. This formula was subsequently changed to $C_{10}H_8O_2$ by Gmelin,[‡] although this change was apparently not based upon any further experimental work. Although I have not as yet had any very considerable quantity of material at my command, I have studied some of its reactions and prepared two well-marked bromine derivatives whose percentage composition necessitates the adoption of the formula $C_{15}H_{12}O_8$.

In the method I have described for the purification of the crude furfurol, after that portion which is volatile with steam has been distilled off, there remains a red viscous oil in the retort, which, on cooling, partially solidifies. If this semi-solid mass is then treated with small quantities of cold alcohol, the red oil, which results, in part at least, from the action of the sodic hydrate upon the furfurol, dissolves, while the greater part of the pyroxanthin is left behind in minute crystals. Occasionally, this viscous residue crystallizes only after the addition of the alcohol and vigorous stirring. The pyroxanthin seems to be more neatly separated, if the furfurol is slightly acidified with acetic acid after separating the alkaline solution before distilling with steam. After the crystals have been well washed with cold alcohol, they are recrystallized from boiling alcohol until the substance has a bright, clear, orange-yellow color. Boiling the alcoholic solution with bone-black facilitates the removal of the red impurities.

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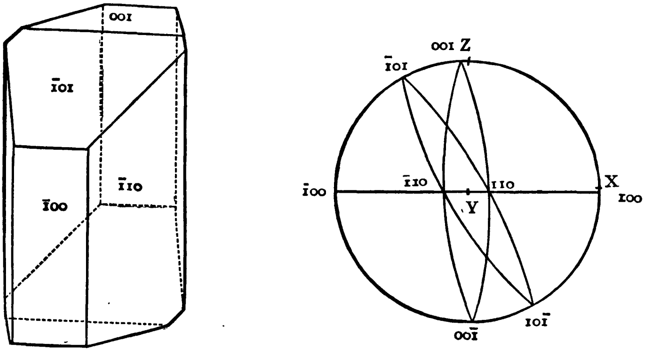
[*] Phil. Mag., [3] xli. 395.

[†] Royal Irish Acad. Proc., 1836, xxxiii. Ann. Chem. u. Pharm., xxi. 143.

[‡] Gmelin's Handbuch, vii. 157.

Pyroxanthin is completely insoluble in water, and very sparingly soluble in ether or carbonic disulphide; in hot alcohol, benzol, or glacial acetic acid it dissolves abundantly, and crystallizes in well-developed forms on cooling. From alcohol it crystallizes in small, brilliant, orange-yellow needles with a blue reflex; from benzol in tolerably large reddish-yellow monoclinic prisms; and from glacial acetic acids in flat radiated needles, which are formed by the development of the prism in the direction of the orthodiagonal. The crystallographic examination which I made of the substance gave the following results.

CRYSTALLINE FORM OF PYROXANTHIN.



Monoclinic System.

Forms observed $\{001\}$ $\{\bar{1}01\}$ $\{100\}$ $\{110\}$.

$a : b : c = 2.748 : 1 : 1.413 \quad ac = 87° 56'$

Angles between Normals.

	Found.	Calculated.
$110 : \bar{1}10$	40° 1′	Fundamental angles.
$\bar{1}01 : 001$	26° 46′	
$\bar{1}01 : \bar{1}00$	61° 10′	
$\bar{1}10 : \bar{1}00$	69° 54′	69° 59′
$\bar{1}10 : \bar{1}01$	80° 25′	80° 30′

For analysis the substance was crystallized from alcohol and dried at 100°.

I. 0.2673 grm. substance gave 0.7341 grm. CO_2 and 0.1279 grm. H_2O.

II. 0.2432 grm. substance gave 0.6690 grm. CO_2 and 0.1141 grm. H_2O.

	Calculated for $C_{15}H_{12}O_3$.	Found. I.	Found. II.	Apjohn and Gregory.
C	75.00	74.91	75.01	74.27
H	5.00	5.31	5.25	5.61

Since the substance was very refractory and needed a high temperature in a stream of oxygen for complete combustion, my results show a sufficiently close agreement with those of Apjohn and Gregory.

This substance melts at 162° and volatilizes with partial decomposition at a higher temperature, although it may be sublimed without difficulty by careful heating in a current of air. In concentrated sulphuric acid it dissolves with an intense purple, and in hydrochloric or hydrobromic acid with a crimson color. From these solutions water precipitates the substance apparently unchanged. In alkaline solutions it is completely insoluble, and by melting caustic potash it is merely carbonized. Bromine attacks it vigorously, and, under certain conditions, forms well-crystallized products.

Dibrompyroxanthintetrabromide, $C_5H_{10}Br_2O_3Br_4$. When pyroxanthin is suspended in ten times its weight of carbonic disulphide, and three and a half parts of bromide diluted with an equal weight of carbonic disulphide are added, the pyroxanthin instantly dissolves and forms a clear deep-red solution. After standing for a short time, clouds of hydrobromic acid are given off, and soon after the separation of a beautifully crystalline substance begins. After twenty-four hours the carbonic disulphide is poured off, and the crystals which have separated are thoroughly washed with ether. For analysis I recrystallized the substance from boiling chloroform and dried it *in vacuo*.

I. 0.5598 grm. substance gave 0.5136 grm. CO_2 and 0.0842 grm. H_2O.

II. 0.6814 grm. substance gave 0.5758 grm. CO_2 and 0.0845 grm. H_2O.

III. 0.3094 grm. substance gave 0.4884 grm. AgBr.*

IV. 0.3128 grm. substance gave 0.4936 grm. AgBr.

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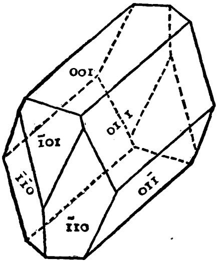
* All the determinations of halogens in this and the subsequent investigations were made according to the method of Carius. In most cases the asbestos

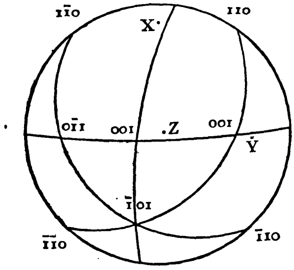
Calculated for $C_{15}H_{10}Br_6O_3$.		Found.			
		I.	II.	III.	IV.
C	25.07	25.02	24.87		
H	1.39	1.67	1.49		
Br	66.85			67.16	67.13

These percentages agree closely with those required by the formula $C_{15}H_{10}Br_6O_3$, and the behavior of the substance is such that it must be considered dibrompyroxanthintetrabromide. It crystallizes in small, brilliant, colorless prisms which belong to the triclinic system. On heating, it is decomposed below 100° with carbonization and the evolution of hydrobromic acid. It is very sparingly soluble in ether or carbonic disulphide; in boiling benzol or chloroform it dissolves quite freely, and the greater part again separates on cooling. In cold alcohol or glacial acetic acid, it is sparingly soluble; but, on warming, it dissolves with decomposition and then forms a yellow solution. In the cold, it is unaltered by concentrated sulphuric acid; on heating, it is carbonized.

A crystallographic study of the substance gave the following results: —

CRYSTALLINE FORM OF DIBROMPYROXANTHINTETRABROMIDE.





Triclinic System.

Forms observed, $\{001\}\ \{011\}\ \{01\bar{1}\}\ \{110\}\ \{\bar{1}10\}\ \{\bar{1}01\}$.

$$a : b : c = 0.733 : 1 : 2.370.$$

$$bc = 74° 43'; \quad ac = 83° 40'; \quad ab = 96° 46'.$$

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filter of Dr. Gooch was used. The great saving of time and labor as well as the increased accuracy attainable by this method renders it invaluable in determinations of this sort.

Angles between Normals.

	Found.	Calculated.
$0\bar{1}1 : \bar{1}\bar{1}0$	. . . . 47° 15′	Fundamental angles.
$0\bar{1}1 : \bar{1}01$	69° 50′	
$0\bar{1}1 : 011$	135° 27′	
$\bar{1}\bar{1}0 : \bar{1}01$	34° 18′	
$\bar{1}\bar{1}0 : \bar{1}10$	76° 57′	
$\bar{1}01 : \bar{1}10$	48° 49′	48° 58′
$\bar{1}10 : 01\bar{1}$	61° 14′	61° 12′
$\bar{1}10 : 011$	58° 6′	57° 41′
$001 : \bar{1}\bar{1}0$	73° 59′	74° 18′
$001 : \bar{1}10$	93° 8′	93° 41′
$001 : 0\bar{1}1$	54° 6′	53° 49′
$001 : 011$	81° 21′	81° 38′
$001 : \bar{1}01$	63° 37′	63° 57′

Bromine when moderately diluted with carbonic disulphide has no further action upon this substance. It is attacked, however, when exposed to the vapors of bromine, and deliquesces rapidly, forming a dark-red syrup, which over lime *in vacuo* gradually solidifies. From this product I have as yet been unable to isolate any substance with characters sufficiently well marked to encourage further study.

Dibrompyroxanthin, $C_{15}H_{10}Br_2O_8$. The subtraction of bromine, on the other hand, gave a beautifully crystalline product with sharply marked characteristics. This substance I first made by the action of phenol. If the dibrompyroxanthintetrabromide is gently warmed with a little phenol, to which sufficient water has been added to keep it liquid, it dissolves, forming a highly colored solution, which is red by transmitted and green by reflected light. If alcohol is then added, it causes the separation of an abundance of fine, felted brilliant-yellow needles, which may be recrystallized from alcohol. This same substance may also be made by boiling the tetrabromide with absolute alcohol, and adding zinc dust or finely powdered metallic antimony. The latter method is perhaps most advantageous, since little or no product is obtained if the phenol solution is too strongly heated, or, if the zinc dust contains a large percentage of oxide. For analysis, the substance was dried at 100° after several recrystallizations from alcohol. The material used in analyses I. and II. was made with phenol, while that used in analysis III. was made with antimony.

I. 0.3816 grm. substance gave 0.6333 grm. CO_2 and 0.0918 grm. H_2O.
II. 0.3137 grm. substance gave 0.2978 grm. AgBr.
III. 0.2577 grm. substance gave 0.2419 grm. AgBr.

Calculated for $C_{15}H_{10}Br_2O_3$.		Found.		
		I.	II.	III.
C	44.22	45.25		
H	2.51	2.67		
Br	40.20		40.40	39.94

The analyses showed that the substance was dibrompyroxanthin, and that it was formed from the bromine derivative already described by the subtraction of bromine.

In hot alcohol it dissolves readily, although in cold it is sparingly soluble. It is quite soluble in ether or carbonic disulphide, and very readily in benzol, chloroform, or glacial acetic acid.

From a solution in warm chloroform, it crystallizes in large, compact, twinned forms of the monoclinic system, which are dichroic. In concentrated sulphuric acid, it dissolves with an intense, pure blue color. This blue solution, on dilution with water, throws down a yellow precipitate, which is apparently the unchanged substance. If quickly heated upon platinum foil, it melts to a perfectly clear yellow liquid; but it is impossible to determine its melting point, since it decomposes and carbonizes when its temperature is more gradually raised. A solution in carbonic disulphide, when mixed with bromine, gradually deposits well-formed crystals of the tetrabromide. This simple substitution product I have not succeeded in making directly from pyroxanthin. In every case where a smaller quantity of bromine was employed, the addition product was still formed, and a part of the pyroxanthin remained unaltered.

I have also studied the action of aqueous bromine, but have not been successful in obtaining any definite products. If pyroxanthin is suspended in water, and bromine gradually added, or the vapors of bromine carried in by a current of air, a white amorphous substance is slowly formed, which is almost insoluble in water, but extremely soluble in other ordinary solvents. By evaporation of such solutions, the substance again separates in an amorphous condition. In alkalies it dissolves, forming a deep-brown solution, from which nothing can be precipitated by the addition of acids.

Since there appeared to be little hope of effecting its purification by ordinary methods, I proceeded to analyze carefully prepared material.

I found, however, that the substance turned brown on standing over sulphuric acid, and the analysis of two different preparations showed conclusively that no constant results could be obtained in this way.

I. 0.3726 grm. substance gave 0.3142 grm. CO_2 and 0.0594 grm. H_2O.
II. 0.2016 grm. of the same preparation gave 0.2773 grm. AgBr.
III. 0.5255 grm. substance gave 0.4142 grm. CO_2 and 0.0734 grm. H_2O.
IV. 0.3853 grm. of the same preparation gave 0.5731 grm. AgBr.

	I.	II.	III.	IV.
C	23.00		21.50	
H	1.77		1.55	
Br		58.53		63.30

These results showed merely that oxidation had taken place together with the substitution of hydrogen by bromine.

On boiling with bromine-water, total decomposition seemed to ensue, and no definite products could be isolated except oxalic acid and a small quantity of a volatile oil which had the odor of bromoform, and gave the characteristic odor of phenyl isocyanide when heated with anilin and alcoholic potash.

Although I have already carried on the investigation of pyroxanthin in several other directions, I have not as yet been able to study the reactions involved as much in detail as I could wish, and I must therefore reserve for a subsequent paper all description of these experiments.

Concerning the origin and mode of formation of the pyroxanthin, I can at present add nothing. Its high melting point, and its general behavior when compared with the properties of the oil from which it is made, lead directly to the conclusion that it results either from polymerization or condensation. Its formula, $C_{15}H_{12}O_8$, naturally suggests a trimolecular polymeric form; the composition of its bromine derivatives, on the other hand, favors rather the view that its molecule is the product of condensation.

Schweizer,* in 1848, prepared from pyroligneous acid an oil to which he gave the name pyroxanthogen, as the substance from which the pyroxanthin was formed. He attempted no explanation of the mode of formation, and made no analysis of his product. Although his description is not very precise, it is sufficient to show that it was a mixture tolerably complex in its nature.

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* Jour. pract. Chem., xliv. 129.

All my own attempts to isolate from the crude furfurol the substance essential to the formation of the pyroxanthin have been unsuccessful. Its separation from the furfurol is a matter of some difficulty, not only on account of the small quantities present, but also since it appears to be closely allied to furfurol. In its boiling point or in its behavior towards reagents, I have as yet found no differences sufficiently well marked to form the basis for a method of separation.

For the present, at least, a more careful study of the pyroxanthin itself would seem to be the most speedy way to discover the mode of its formation.

MUCOBROMIC ACID.

Mucobromic acid was first made by Schmelz and Beilstein,* in 1865, by the action of bromine and water upon pyromucic acid. They found its salts so unstable that they made little attempt to isolate them, but confined themselves chiefly to the study of the decomposition which ensued when it was boiled with alkalies, and of the reaction effected by argentic oxide.

They found that the acid was rapidly decomposed when boiled with baric hydrate, that bromacetylen was set free, and that baric carbonate was precipitated. In solution, they found, beside baric bromide, a sparingly soluble barium salt, to which they gave the name, baric muconate, and the formula, $BaC_4O_3 \cdot H_2O$. This formula was, however, based upon a single barium and two water determinations. They also prepared the free muconic acid, but made no further study of it than to establish the fact that it was a crystalline solid readily soluble in water, and that its lead salt was insoluble. They expressed the reaction which they supposed had taken place by the equation: —

$$2\ C_4H_2Br_2O_3 + H_2O = C_4H_2O_3 + C_2HBr + 2\ CO_2 + 3\ HBr.$$

They also found that mucobromic acid was attacked when boiled with argentic oxide and water, that argentic bromide was formed, and at the same time a silver salt quite insoluble in water. This silver salt, according to their calculations of the analytical results which they obtained, had the formula $C_7H_2Br_3Ag_3O_5$, and they regarded this as an intermediate product standing between mucobromic and muconic acids. The acid was found to be a crystalline solid, which appeared to give bromacetylen and muconic acid when heated with baric hydrate. The reaction with argentic oxide they wrote: —

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* Ann. Chem. u. Pharm., Suppl., iii. 276.

$$2\ C_4H_2Br_2O_3 + 2\ Ag_2O = C_7H_2Br_3Ag_3O_5 + AgBr + H_2O + CO_2.$$

In the course of the investigations upon mucic acid and its derivatives, which were begun in Limpricht's* laboratory in 1868, mucobromic acid received more or less attention. Although it was found to be the only product when pyromucic acid was treated with water and an excess of bromine at ordinary pressures, Limpricht and Delbrück showed that it was completely decomposed when heated in a sealed tube to 120° with bromine and water, provided that three molecules of bromine, at least, were used to one of mucobromic acid. As products of the decomposition, they found, beside carbonic dioxide and hydrobromic acid, tribromethylenbromide, C_2HBr_5, perbromathylenbromide, C_2Br_6, tetrabrombutyric (?) acid, $C_4H_4Br_4O_2$, and dibromfumaric (?) acid, $C_4H_2Br_2O_4$. The marks of interrogation appear in Limpricht's original paper. Limpricht and Lessing also found in one experiment that, by the reduction of mucobromic acid, a liquid was formed which boiled at about 120° and contained 84.8 per cent of carbon, 8.8 of hydrogen, and the remaining 6.4 per cent was oxygen. They were, however, unable to repeat the experiment with a like result.

In attempting the preparation of mucobromic acid, Mr. O. R. Jackson and I found that we were unable to obtain a satisfactory yield by following the method given by Schmelz and Beilstein or by Limpricht. Schmelz and Beilstein say that the quantity of water taken is not a matter of indifference, but neither they nor Limpricht make any specific statements as to the amount which they found to be most advantageous. They agree, however, that the bromine should be added slowly as long as it is taken up in the cold, that the solution should then be heated and bromine added as long as the color continues to disappear.

According to this method, we were unable to get more than 25 per cent of the theoretical yield; and at the same time we were obliged to use quite a large excess over the amount of bromine calculated from the equation: —

$$C_5H_4O_3 + 4\ Br_2 + 2\ H_2O = C_4H_2Br_2O_3 + CO_2 + 6\ HBr.$$

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* Berichte d. deutsch. chem. Gesellsch., ii. 211; iii. 90, 671; iv. 805; Zeitschr. für Chem., 1869, 599; Ann. Chem. u. Pharm., clxv. 253.

We soon found that our yield was greatly increased and the excess of bromine proportionately decreased if the bromine was added rapidly. Later, when it was found that a low temperature was essential to the formation of mucochloric acid, the pyromucic acid and water were cooled with ice until the bromine had all been added, but the yield was not perceptibly affected.

We have obtained the best results by the following method: Pyromucic acid is suspended in ten times its weight of water contained in a flask fitted with reverse cooler and drop-funnel. The calculated amount of bromine is then rapidly added, cooling only so far as may be necessary to avoid loss of bromine. After the bromine is all added, the flask is heated, and the liquid kept boiling for ten or fifteen minutes. The solution may then be allowed to crystallize direct, although we have usually evaporated it until the hydrobromic acid began to volatilize in abundance before allowing it to cool. In either case the crystals should be well washed with cold water and recrystallized from boiling water. In this way we have found it easy to obtain 70 per cent and over of the theoretical yield.*

The acid recovered from the mother liquors is usually very dark colored, and it cannot be purified by recrystallization from water either with or without the addition of bone-black. We have found, however, that such an acid may be obtained perfectly white by one or two recrystallizations from dilute sulphuric acid (1 : 4).

As to the properties of mucobromic acid, we can only confirm the statements of Schmelz and Beilstein. It crystallizes ordinarily from water in irregular leafy aggregates, from acid solutions or from certain other solvents in distinct rhombic plates. From a solution in concentrated hydrobromic acid, we have frequently obtained it in large compact crystals, with edges 10 to 12 mm. in length, but so striated as to render measurement impossible. It is sparingly soluble in cold water, very readily in hot water, in alcohol or in ether. In benzol or carbonic disulphide, it is very sparingly soluble in the cold, but dissolves quite readily on heating. Chloroform takes up a little when hot, most of which it deposits on cooling. In warm concentrated sulphuric acid, it dissolves freely, and, if not too strongly heated, crystallizes out on cooling or on dilution. It melts at 120–121°, and at a higher temperature it distils in part unchanged.

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* Under conditions favorable to complete crystallization from the concentrated hydrobromic acid which forms the mother liquors, we have obtained 78 per cent.

The following analyses may serve to show the purity of the material used in the course of the following investigations: —

I. 0.7840 grm. substance gave 0.5390 grm. CO_2 and 0.0720 grm. H_2O.
II. 0.9326 grm. substance gave 0.6340 grm. CO_2 and 0.0712 grm. H_2O.
III. 0.2347 grm. substance gave 0.3421 grm. AgBr.
IV. 0.2331 grm. substance gave 0.3410 grm. AgBr.

Calculated for $C_4H_2Br_2O_3$.		Found.			
		I.	II.	III.	IV.
C	18.60	18.75	18.55		
H	0.77	1.02	0.85		
Br	62.02			62.03	62.25

Salts of Mucobromic Acid.

Schmelz and Beilstein found that mucobromic acid decomposed baric carbonate, and that the barium salt thus formed was readily soluble in water, although it was decomposed during the spontaneous evaporation of the solution. As it seemed a matter of some interest to determine whether mucobromic acid was capable of forming salts, Mr. O. R. Jackson and I pursued the investigation one step further.

Baric Mucobromate, $Ba(C_4HBr_2O_3)_2$. We found that an aqueous solution of mucobromic acid dissolved baric carbonate readily, that the solution on standing soon turned brown, deposited a brownish flocculent precipitate, and contained then a baric bromide in abundance. On heating, the same change took place more rapidly, and when the solution was boiled a substance was volatilized with the steam which had a sharp, acrolein-like odor, and reduced silver oxide on heating. Although this change was rapid near 100°, we found that it was sufficiently slow at 50–60° to allow the preparation of a solution saturated at this temperature which on cooling with vigorous stirring deposited crystals of the barium salt. The mucobromic acid was suspended in very little water, the whole warmed to 50–60°, baric carbonate added in excess, and the solution filtered and cooled as rapidly as possible. Even with these precautions we found it difficult to saturate the acid completely without bringing about decided decomposition. The salt, therefore, usually contained more or less free acid, from which it could be completely freed by washing with ether. The salt when dried *in vacuo* over sulphuric acid hardly lost weight at 100°, but when heated a few degrees higher it turned brown and gave out the sharp, penetrating odor mentioned above. Analyses I. and II. were made with a preparation crystallized from water without subsequent washing, III., IV., and V. with substance washed with ether.

I. 0.9479 grm. gave 0.5018 grm. CO_2 and 0.0547 grm. H_2O.
II. 0.3434 grm. gave, on ignition with H_2SO_4, 0.1165 grm. $BaSO_4$.
III. 0.4186 grm. gave, on ignition, 0.1482 grm. $BaSO_4$.
IV. 0.5747 grm. gave, on ignition, 0.2030 grm. $BaSO_4$.
V. 0.7638 grm. gave, on ignition, 0.2695 grm. $BaSO_4$.

Calculated for $Ba(C_4HBr_2O_3)_2$.		Found.				
		I.	II.	III.	IV.	V.
C	14.74	14.44				
H	0.30	0.63				
Ba	21.04		19.95	20.82	20.77	20.74

This salt is readily soluble even in the cold water, and soluble also in alcohol. On boiling its aqueous solution, the decomposition described above ensues, with the evolution of carbonic dioxide. This reaction has not yet been farther studied.

Argentic Mucobromate, $AgC_4HBr_2O_3$. The silver salt may be made by adding a concentrated solution of argentic nitrate to a solution of the barium salt. Since it is quite soluble even in cold water, it is better to use, instead of the barium, the calcium salt, in order to facilitate washing. It is precipitated in fine, felted needles, which blacken quite rapidly on exposure to diffused light, and are decomposed at once on moistening with alcohol or warming with water; argentic bromide is formed, together with some metallic silver. This substance was dried *in vacuo* for analysis: —

I. 0.3601 grm. gave 0.1862 grm. AgBr.
II. 0.5640 grm. gave 0.2903 grm. AgBr.

Calculated for $AgC_4HBr_2O_3$.		Found.	
		I.	II.
Ag	29.59	29.70	29.56

Ethyl Mucobromate. The ethyl ether of mucobromic acid may readily be made by saturating its solution in absolute alcohol with hydrochloric acid, or more conveniently by warming this solution with concentrated sulphuric acid. If considerable sulphuric acid be used, the ether often crystallizes out on standing in large, well-formed crystals, otherwise it is precipitated by the addition of water and washed with a dilute solution of sodic carbonate. The crude product contains impurities which can be removed only by repeated recrystallization from alcohol. This recrystallization is more conveniently accomplished if the moderately saturated solution is cooled to 0°. The ether crystallizes in large, transparent forms of the monoclinic system, which melt at 50–51° and boil at 255–260° with partial decomposition. When slightly warmed it has a pungent, aromatic odor.

The analysis of substance dried *in vacuo* over sulphuric acid gave:

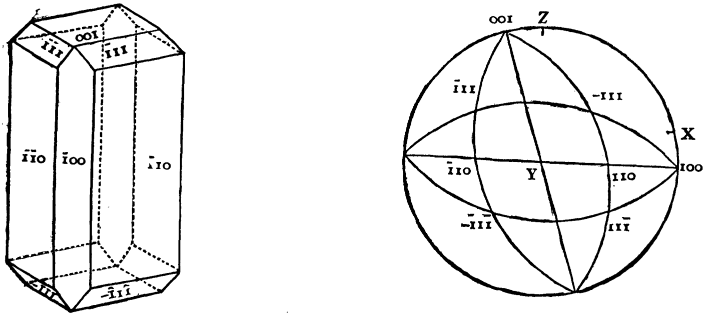
I. 0.8583 grm. substance gave 0.7933 grm. CO_2 and 0.1686 grm. H_2O.

II. 0.7000 grm. substance gave 0.6432 grm. CO_2 and 0.1377 grm. H_2O.

Calculated for $C_4HBr_2O_3 . C_2H_5$.		Found.	
		I.	II
C	25.17	25.24	25.05
H	2.10	2.18	2.18

Mr. Mabery has studied the crystalline form of this substance, and obtained the following results: —

CRYSTALLINE FORM OF ETHYL MUCOBROMATE.



Monoclinic System.

Forms observed, — $\{\bar{1}11\}$ $\{111\}$ $\{100\}$ $\{001\}$ $\{110\}$.

$a : b : c = 1.053 : 1 : 1.221$; $ac = 78° 27'$.

Angles between Normals.

	Found.	Calculated.
$\bar{1}\bar{1}1 : \bar{1}11$	82° 11′	Fundamental angles.
$\bar{1}\bar{1}0 : \bar{1}10$	92° 7′	
$\bar{1}11 : \bar{1}10$	32° 56′	
$\bar{1}11 : 001$	64° 53′	64° 46′
$\bar{1}11 :–111$	72° 11′	71° 50′
$001 :–111$	52° 44′	52° 53′
$1\bar{1}0 :–111$	29° 8′	29° 17′
$110 : \bar{1}10$	87° 50′	87° 53′
$110 : 001$	81° 50′	82° 1′
$\bar{1}10 : 001$	98° 4′	97° 59′
$\bar{1}10 : \bar{1}00$ *	45° 37′	46° 4′

Action of Phosphoric Pentabromide and Acetylchloride.

Mr. O. R. Jackson studied with me the behavior of mucobromic acid towards phosphoric pentabromide and acetylchloride.

Mucobromylbromide. When mucobromic acid is mixed with about four times its weight of phosphoric pentabromide, and the mixture heated for a short time at 110–115°, a quiet reaction sets in, the mass becomes liquid, and water then precipitates a heavy red oil, which after thorough washing with water gradually solidifies at ordinary temperatures, or immediately if cooled to 0°. This substance is very soluble in alcohol, ether, benzol, chloroform, or carbonic disulphide, but crystallizes well from a solution in a little hot alcohol when this is cooled to 0°. After repeated crystallization from alcohol, it forms small, slender prisms, which melt at 55–56°, and have the percentage composition corresponding to mucobromylbromide.

I. 0.6643 grm. substance gave 0.3755 grm. CO_2 and 0.0374 grm. H_2O.

II. 0.2598 grm. substance gave 0.4573 grm. AgBr.

III. 0.2252 grm. substance gave 0.3964 grm. AgBr.

Calculated for $C_4HBr_3O_2$.		Found. I.	Found. II.	Found. III.
C	14.96	15.41		
H	0.31	0.63		
Br	74.77		74.89	74.89

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* The form {100} was observed upon two or three individuals only, and the reflections were imperfect.

The behavior of this substance towards alkalies is especially characteristic. The reaction may best be observed when baric hydrate is cautiously added to a dilute alcoholic solution. An intense indigo-blue color is at once developed, which, however, soon passes through green to reddish yellow, with the simultaneous formation of a brown-red, flocculent precipitate. The same brown precipitate is formed when the mucobromylbromide is boiled in an excess of baric hydrate; but the two products which are most characteristic of the decomposition of mucobromic acid under the same conditions,* bromacetylen and malonic acid, are formed in such small quantities that they may easily be overlooked. This peculiar behavior led us to suppose at first we had not the simple bromanhydride of mucobromic acid in our hands, but that an hydroxyl group outside the carboxyl had been replaced. A more careful study showed, however, that such was not the case. Although this mucobromylbromide is apparently little affected even by hot water, on boiling it is gradually decomposed, and the solution then contains mucobromic acid (m. pt. 120–121°). Absolute alcohol decomposes it with more difficulty; still, after several hours' boiling with reverse cooler, on evaporating the excess of alcohol and cooling strongly, crystals separated which had the characteristic form of the ethylmucobromate, and which melted at 51° after recrystallization from alcohol.

Mucobromic Acetanhydride. When mucobromic acid is heated in a sealed tube for several hours with an excess of acetylchloride at 120°, or when it is heated under ordinary pressure with acetic anhydride, a substance is formed, which is very soluble in alcohol, ether, or chloroform, and which may be purified by precipitation by water from its alcoholic solution. It falls as a colorless oil, which gradually solidifies in slender, dendritic needles, which melt at 53–54°.

0.9015 grm. gave 0.8050 grm. CO_2 and 0.1290 grm. H_2O.

Calculated for $C_4HBr_2O_3 . C_2H_3O$.		Found.
C	24.00	24.36
H	1.33	1.59

That the acetyl group enters the carboxyl in this case is shown by the behavior of ethylmucobromate to acetylchloride. After several hours' heating, with an excess of acetylchloride, at 140–150°, the ether was found to be unaltered. The substance which was obtained crystallized in the form of the ethyl-ether, melted at 50°, and upon analysis proved to contain the required percentage of bromine.

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* Cf. p. 188 *et seq.*

0.2720 grm. gave 0.3600 grm. AgBr.

Calculated for $C_4HBr_2O_3 . C_2H_5$.		Found.
Br	55.94	56.32

Action of Bromine.

Limpricht and Delbrück studied in detail the action of bromine and water upon mucobromic acid, but they made no experiments with dry bromine. It therefore seemed advisable to investigate the action of dry bromine; since the reactions in this case would naturally be less complicated than with aqueous bromine, and on that account might prove to be of more service in determining the constitution of mucobromic acid. In my first experiments I employed equal molecules of bromine and mucobromic acid, but soon found that one molecule of bromine sufficed for the complete decomposition of nearly two molecules of mucobromic acid, although the products of the reaction were essentially the same whether the bromine was used in excess or not.

At 100°, very little action was noticeable; at 120–130°, the action was marked, but so slow that the temperature was raised to 140°. Here the reaction ran rapidly, and after two hours the bromine had disappeared. On cooling, the tubes were filled with long, prismatic crystals, which were permeated with a nearly colorless oil. On opening the tubes, hydrobromic acid gas escaped in abundance, and with it could be detected a comparatively small amount of carbonic dioxide. The partially solidified product of the reaction was treated with small quantities of cold water. The greater part of the prismatic crystals were in this way carried into solution; while the oil, in which a small quantity of crystals were yet to be seen, was left undissolved. This aqueous solution, upon evaporation, left a white, crystalline acid, very soluble in water, which for purification was converted into the barium salt. Before neutralizing the aqueous solution with baric carbonate, I found it best to evaporate to dryness, and take up a second time with a little cold water, in order to remove the small quantity of undecomposed mucobromic acid which often was present. The barium salt was precipitated several times from aqueous solution by alcohol, and finally crystallized from water by evaporation. Thus purified, it formed brilliant, transparent, rhombic plates, which lost water in desiccator slowly, but which I was unable to dehydrate perfectly by heat, either at ordinary pressures or *in vacuo*, without causing partial decomposition. The analysis of the air-dried salt gave percentages required by a barium salt of dibrommaleic acid containing two molecules of water of crystallization.

I. 0.8687 grm. of substance lost, at 120°, 0.0624 grm. H_2O. Of this dried salt, 0.4145 grm. gave, by ignition, 0.2341 grm. $BaSO_4$.
II. 0.5780 grm. of air-dried salt gave, by ignition, 0.3010 $BaSO_4$.

Calculated for $BaC_4Br_2O_4 . 2 H_2O$.		Found.	
		I.	II.
Ba	30.78	30.86	30.63
H_2O	8.09	7.07	

This salt is hardly more soluble in boiling water than in cold; in dilute alcohol, it is almost insoluble. The solubility in water was determined according to the method of V. Meyer.

I. 7.1377 grm. of a solution saturated at 19° gave, on evaporation with H_2SO_4 and ignition, 0.2296 grm. $BaSO_4$.
II. 6.9649 grm. of a solution saturated at 19° gave 0.2249 grm. $BaSO_4$.

An aqueous solution saturated at 19°, therefore, contains of the anhydrous salt the percentages: —

I.	II.
5.65	5.67

The silver salt could best be made by the precipitation of a solution of the free acid by argentic nitrate. From dilute solution, it separated in long, flat needles; from concentrated solutions, it was precipitated in small prisms. It proved to be almost insoluble even in hot water. The dry salt exploded violently on heating, or by percussion.

0.6311 grm. of the salt, dissolved in dilute nitric acid, gave 0.4859 grm. AgBr.

Calculated for $Ag_2C_4Br_2O_4$.		Found.
Ag	44.27	44.22

The lead salt fell as a crystalline precipitate upon the addition of plumbic acetate even to a dilute solution of the free acid.

The acid was liberated from the pure barium salt by the addition of normal sulphuric acid, in quantity insufficient for complete precipitation; the aqueous solution was allowed to evaporate spontaneously; and the acid was then separated from the excess of barium salt by means of ether free from alcohol. Prepared in this way, the acid formed a mass of indistinct, aggregated needles, extremely soluble in water, ether, or alcohol; and almost insoluble in boiling chloroform, benzol, ligroin, or carbonic disulphide. From a mixture of ether and chloroform, it could be crystallized in the form of fine, felted needles.

After standing in desiccator, the acid gave on analysis too high a percentage of bromine (I.). It was therefore washed with chloroform, the excess of chloroform evaporated in a paraffine desiccator according to Liebermann's suggestion; but the percentage of bromine remained essentially unaltered (II.). I therefore dissolved the acid in hot water, allowed the solution to evaporate spontaneously, and dried by exposure to the air alone, but failed to alter its composition (III.). Subsequently I dissolved the pure anhydride described below in hot water, and found that the acid obtained by spontaneous evaporation of this solution when air-dried also contained more bromine than the formula of the acid required (IV.).

I. 0.2050 grm. substance gave 0.2860 grm. AgBr.
II. 0.2305 grm. substance gave 0.3200 grm. AgBr.
III. 0.2150 grm. substance gave 0.3000 grm. AgBr.
IV. 0.2500 grm. substance gave 0.3475 grm. AgBr.

Calculated for $C_4H_2Br_2O_4$.		Found.			
		I.	II.	III.	IV.
Br	58.38	59.37	59.08	59.38	59.15

From these experiments it would appear that the acid, even at ordinary temperatures, is partially converted into its anhydride. This change goes on rapidly at temperatures near 100°, so that it is impossible to obtain constant melting points. The preparations analyzed melted at 120–125° when warmed with ordinary rapidity. The acid was but slightly volatile with steam, but could be distilled with greatest readiness with the vapor of concentrated hydrobromic acid.

From this acid the anhydride could be obtained without difficulty in a pure state, by heating to 120° in a current of dry carbonic dioxide. The sublimation began at 100°, or possibly lower, but became rapid at 115–120°. The anhydride condensed in lustrous, flattened needles, which melted at 114–115°. In cold water it dissolved but slowly; in alcohol, ether, benzol, ligroin, chloroform, or carbonic disulphide, it was readily soluble.

I. 0.3672 grm. gave 0.2510 grm. CO_2 and 0.0010 grm. H_2O.
II. 0.2630 grm. gave 0.3870 grm. AgBr.

Calculated for $C_4Br_2O_3$.		Found.	
		I.	II.
C	18.75	18.65	
H	—	0.02	
Br	62.50		62.61

The aqueous solution obtained by treating the original product from the action of bromine with cold water, therefore, contained mainly an acid of the composition of dibrommaleic acid.

In the mother liquors from the baric dibrommaleate there appeared to be a trace of a more soluble barium salt beside baric bromide; but its quantity was too small to admit of separation and analysis.

The oily residue left undissolved by water gradually solidified upon standing. Cold chloroform dissolved the greater portion of it, leaving a small quantity of short, prismatic crystals. Upon evaporation of the chloroform, an oil was left, which gradually solidified in masses of radiated prisms, contaminated with a small quantity of an oily impurity whose nature could not further be determined. After several crystallizations from alcohol, this substance melted at 55–56°, and when treated with baric hydrate gave the characteristic reactions of mucobromylbromide. It was still further identified by analysis.

0.2280 grm. substance gave 4000 grm. AgBr.

Calculated for $C_4HBr_3O_3$.		Found.
Br	74.77	74.68

The prismatic crystals, which were sparingly soluble in cold water and chloroform, were recrystallized from hot water, and showed then the characteristic properties of ordinary dibromsuccinic acid. On heating, they remained unaltered till the temperature had risen to over 200°; at a somewhat higher point, they had completely volatilized. The sublimate condensed in the colder portions of the tube in oil drops, which gradually solidified. The melting point of the solid thus obtained, after pressing with filter paper, was found to be 126°. According to Fittig and Petri,† the sublimate formed under the same conditions from dibromsuccinic acid has the melting point of monobrommaleic acid (128°). The quantity of dibromsuccinic acid formed in this reaction was quite small.

0.2855 grm. substance gave 0.3880 grm. AgBr.

Calculated for $C_4H_4Br_2O_4$.	Found.
57.97	57.83

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† Ann. Chem. u. Pharm., cxcv. 58.

When the original product of the reaction was treated at once with dry chloroform, the greater part was instantly carried into solution; and the dibromsuccinic acid, together with a small quantity of mucobromic acid, were left undissolved. The filtered chloroform solution, when shaken with a few drops of water, gradually solidified with separating crystals of dibrommaleic acid; so that the original product must have contained the dibrommaleic acid as anhydride.

The two main products of the reaction were, therefore, dibrommaleic anhydride and mucobromylbromide. The relative weights of these two products were such as to suggest at once the equation: —

$$2\ C_4H_2Br_2O_3 + Br_2 = C_4H_2Br_2O_4 + C_4HBr_3O_2 + HBr,$$

when the dibrommaleic acid would readily pass into its anhydride. The weights obtained in successive preparations were, however, found to vary so much that I am inclined to consider the anhydride as the direct product of the reaction, and the mucobromylbromide a secondary product formed by the action of the hydrobromic acid set free. In either case, the formation of dibromsuccinic acid can hardly be explained without assuming a reducing action of the hydrobromic acid, like that which is normal to hydriodic acid. Although reductions of this sort by the action of hydrobromic acid have seldom been noticed, the conversion of tartaric acid into monobromsuccinic acid by this means, noticed by Kekulé* in 1864, would seem to be perfectly analogous.

Dibrommaleic Acid of Kekulé.

In 1864 Kekulé † found among the products of the action of bromine and water upon succinic acid an acid, $C_4H_2Br_2O_4$, to which he gave the name dibrommaleic acid. It formed white, clustered needles, which were extremely soluble in water, alcohol, or ether, and melted at 112°; at higher temperatures the acid distilled apparently unchanged, and it volatilized readily with steam. For the further characterization of the acid, Kekulé made the silver and lead salts. The silver salt could be precipitated from an aqueous solution of the acid, by the addition of argentic nitrate; and, according to the concentration of the solution, it appeared as a granular, crystalline precipitate, or in slender, glistening needles. The dry salt exploded violently by heat or percussion. The lead salt was thrown down by the addition of plumbic acetate to an aqueous solution of the acid, and when air-dried it was found to contain a molecule of water.

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* Ann. Chem. u. Pharm., cxxx. 30.

† Ann. Chem. u. Pharm., cxxx. 1.

Since its discovery by Kekulé, the acid prepared in this way has been mentioned but twice, as far as I know; and these notices contain no additional facts which could serve to assist in its identification. Bourgoin * gives its melting point as 110°, and asserts that it distils unaltered. Fittig and Petri,† in their attempts to prepare the tribromsuccinic acid, which had been described by Bourgoin, obtained dibromsuccinic acid and a substance crystallizing in hemispherical aggregations, which, from their melting point (112°) and volatility with steam, they recognized as dibrommaleic acid.

In 1873 Limpricht and Delbrück ‡ described an acid of the same composition, which they made by the action of bromine and water upon mucobromic acid. They found it difficult of purification; and, in their study of it, they were to all appearance hampered by lack of material. The acid melted at 108–120°, and by sublimation it was converted into its anhydride, $C_4Br_2O_3$, which melted at 95–120°. The barium salt they obtained in colorless, tabular crystals, to which they assigned the formula, $BaC_4Br_2O_4.2H_2O$. The silver salt they found to be insoluble; but it did not explode either by heat or percussion. They assumed, apparently without hesitation, that this acid was isomeric with that of Kekulé, and therefore named it dibromfumaric acid.

The acid made by the action of bromine upon mucobromic acid, which I have just described, agreed in most respects closely with the acid described by Kekulé; and yet the higher melting point and the ready formation of the anhydride rendered a further comparison necessary in order to settle the question of identity.

In the preparation of dibrommaleic acid, I followed in general the method of Kekulé; but, since this was to be the main product of the reaction, I was obliged to use a greater proportion of bromine and water, in order to get any considerable yield.

I obtained good results by using to one part of succinic acid two of water and four of bromine, and heating twenty hours at 140°. The mother liquors from which the greater part of the dibromsuccinic acid had been separated were distilled, the distillate neutralized with baric carbonate, and the baric dibrommaleate precipitated from the filtered

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* Bull. Soc. Chim. [2], xxi. 404; xxii. 443.

† Ann. Chem. u. Pharm., cxcv. 76.

‡ Ann. Chem. u. Pharm., clxv. 294.

solution. After several precipitations from aqueous solution by alcohol, it was crystallized from water by evaporation, and dried by exposure to the air. The salt could not be distinguished in outward appearance from that made from mucobromic acid.

I. 2.4931 grm. of air-dried salt lost in weight, at 125–130°, 0.2136 grm. 0.7670 grm. of this dried salt gave, on ignition with H_2SO_4, 0.4393 grm. $BaSO_4$.

II. 0.5899 grm. air-dried salt gave 0.3102 grm. $BaSO_4$.

Calculated for $C_4Br_2O_4Ba.2H_2O$.		Found.	
		I.	II.
Ba	30.78	30.79	30.91
H_2O	8.09	8.15	

The solubility of this salt was determined according to the method of V. Meyer.

8.9481 grm. of a solution saturated at 20° gave 0.2912 grm. $BaSO_4$.

The aqueous solution saturated at 20°, therefore, contains 5.71 per cent of the anhydrous salt.

From this barium salt, the free acid was made in the manner above described. In its behavior towards solvents, it resembled perfectly the acid made from mucobromic acid, and it melted between 120° and 123°. This acid I did not analyze; but the analyses published by Kekulé show too high a percentage of bromine, and in this respect do not differ essentially from those I have given above.

Calculated for $C_4H_2Br_2O_4$.		Found by Kekulé.	
		I.	II.
Br.	58.38	58.98	59.08

By heating this acid in a stream of carbonic dioxide, the anhydride could readily be made in appearance and behavior perfectly identical with the compound already described, and melting at 114°–115°.

I. 0.4160 grm. substance gave 0.2860 gr. CO_2 and 0.0032 grm. H_2O.

II. 0.2840 grm. substance gave 0.4165 grm. AgBr.

Calculated for $C_4Br_2O_3$.		Found.	
		I.	II.
C	18.75	18.75	
H	—	0.10	
Br	62.50		62.34

The identity of the dibrommaleic acids made by the action of dry bromine upon mucobromic acid and aqueous bromine upon succinic is thus sufficiently established. They each give an anhydride melting at 114–115°; their barium salts have the same composition, $BaC_4Br_2O_4 . 2H_2O$; and the solubility of these two salts in water is the same, the saturated aqueous solution containing in one case 5.66 per cent of the anhydrous salt at 19°, in the other 5.71 per cent at 20°.

Although I have several times tried the action of bromine and water upon mucobromic acid, according to the method of Limpricht and Delbrück, I have not as yet submitted the product obtained in this way to any very extended investigation. In all qualitative reactions it is identical with the acid I have described; and, considering the mode of its formation, one can hardly doubt its identity. Moreover, with regard to the slight differences which would seem to have induced Limpricht and Delbrück to consider their acid isomeric with Kekulé's, I have been unable to confirm their observations. The melting point (95–120°) given by them for the anhydride does not give confidence in the purity of their material. The higher percentage of barium (31.9) * which they found in their barium salt would be in no way at variance with my results, even if its purity were granted, since the material they analyzed had been dried *in vacuo* (over sulphuric acid?), and my own experiments have shown that it slowly effloresces under these conditions.

Although the foregoing facts seemed to warrant the conclusion that the dibrommaleic acid of Kekulé belonged to the maleic series, inasmuch as the anhydride was the direct product of the reaction of bromine upon mucobromic acid, still I thought it advisable to prove this directly, more especially since all analogy pointed to the formation of a derivative of fumaric acid under the conditions essential to its preparation from succinic acid. I therefore dissolved in water the pure anhydride prepared from succinic acid, neutralized the solution with baric carbonate, precipitated the barium salt by alcohol, and recrystallized it from water. This salt proved to be identical with that which was obtained directly from the acid.

0.7525 grm. of the air-dried salt lost on heating to about 120° 0.0581 grm.; 0.6933 grm. of this dried salt gave 0.3922 grm. $BaSO_4$.

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* Limpricht and Delbrück erroneously calculated the percentage of barium in the salt $BaC_4Br_2O_4.2H_2O$ as 31.9 per cent, instead of 30.78, and therefore gave the same formula.

Calculated for $BaC_4Br_2O_4 . 2H_2O$.		Found.
Ba	30.78	30.69
H_2O	8.09	7.72

The solubility was also determined by the method of V. Meyer.

7.6833 grm. of the solution saturated at 19°.5 gave, on evaporation with H_2SO_4 and ignition, 0.2446 grm. $BaSO_4$.

An aqueous solution saturated at 19°.5 contained therefore 5.58 per cent of the anhydrous salt.

This proves that dibrommaleic acid may be carried unchanged through its anhydride, and that it consequently belongs to the maleic series, unless, indeed, its behavior is radically changed by the complete replacement of its hydrogen by bromine. That such is not the case has recently been shown by Bandrowski,* who has discovered an acid of the same composition, which is undoubtedly dibromfumaric acid. This acid melts at 219–220°, and by distillation is converted into dibrommaleic acid.

Mucobromic Acid with Oxidizing Agents.

The close connection between mucobromic acid and dibrommaleic, as shown by its behavior when heated with bromine, naturally suggested the direct conversion of the one into the other by oxidation.

An aqueous solution of chromic acid does not act upon mucobromic acid at ordinary temperatures, even after standing for weeks. On warming, carbonic acid is freely given off, and at the same time a sharp, acrolein-like odor is noticed. If one atom of oxygen is employed for every molecule of mucobromic acid, a portion of the mucobromic acid seems to be completely destroyed, while nearly one half of it remains unaltered, and may be extracted with ether after the reaction is completed. When two atoms of oxygen are taken, but little mucobromic acid escapes oxidation; but I have been unable to isolate well-marked products of the reaction, in any considerable quantities. When the solution is distilled, the substance possessing the sharp, pungent odor passes over with the steam. It is quite soluble in water, although not in all proportions, and its aqueous solution reduces silver energetically from the oxide even in the cold. Although this is the most striking product of the oxidation, it is formed in such small quantities that I have as yet been unable to study it further. After this volatile product has been distilled off, but a trace of organic acid can be extracted from the retort residue by ether. This acid is chiefly mucobromic; but with it I have found dibrommaleic acid in quantity barely sufficient for the recognition of its barium salt under the microscope when precipitated from aqueous solution by alcohol. The oxidation with nitric acid gives somewhat better results. When mucobromic acid is boiled with ten times its weight of nitric acid of sp. gr. 1.20, carbonic dioxide is slowly given off, the escaping gas renders a solution of argentic nitrate turbid, and yet, if the heat is continued for several hours, a considerable portion of the mucobromic acid is found to be converted into dibrommaleic acid. In one experiment I obtained, after several hours' boiling, from 5 grm. of mucobromic acid 2.3 grm. of baric dibrommaleate and 1.5 grm. of unaltered mucobromic acid. This corresponds to nearly forty per cent of the theoretical yield of dibrommaleic acid from the mucobromic acid which entered into the reaction. Stronger nitric acid oxidizes more rapidly, but the yield of dibrommaleic acid is smaller; if much more dilute acid is used, the mucobromic acid is hardly altered.

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* Berichte der deutsch. chem. Gesellsch., xii. 2213.

Precisely the same effect is produced by long boiling with bromine water, carbonic dioxide being evolved as before, and the yield of dibrommaleic acid remaining essentially the same. The identity of the acid made by bromine water was established by the analysis of the barium salt. This salt was precipitated several times from aqueous solution by alcohol, recrystallized from water, and contained then the required percentage of barium.

0.5493 grm. of the air-dried salt gave 0.2887 grm. $BaSO_4$.

	Calculated for $BaC_4Br_2O_4.2H_2O$.	Found.
Ba	30.78	30.90

Limpricht found that mucobromic acid was the only product when pyromucic acid suspended in water was treated with an excess of bromine at ordinary pressures. Since mucobromic acid is itself converted into dibrommaleic acid by boiling it with bromine water, it follows that the latter acid must of necessity be formed in the preparation of mucobromic acid. For its detection, the mother liquors, from which the mucobromic acid had been separated as completely as possible, were distilled. The distillate, consisting chiefly of concentrated hydrobromic acid (b. pt. 126°) was partially neutralized with potassic carbonate, and thoroughly shaken out with ether. The residue left on evaporation of the ether was taken up with water, and the acid solution saturated with baric carbonate. Alcohol precipitated from the filtered solution baric dibrommaleate in characteristic form. For analysis, the salt was recrystallized from water, and dried by exposure to the air.

0.4709 grm. of this salt gave 0.2516 grm. $BaSO_4$.

Calculated for $BaC_4Br_2O_4.2H_2O$.		Found.
Ba	30.78	31.41

Since the percentage of barium was found to be too high, for further identification the acid was set free, and converted into the anhydride by sublimation. This crystallized in the characteristic flattened needles, which melted at 114°. The quantity of dibrommaleic acid formed in the ordinary preparation of mucobromic acid is very inconsiderable, and amounted in one case to about one per cent of the pyromucic acid employed. The quantity must, however, of necessity be very variable.

The oxidation of mucobromic acid by means of argentic oxide was investigated by Schmelz and Beilstein. They gave to the chief product of the reaction the formula, $Ag_3C_7H_2Br_3O_5$; but it is evident from an inspection of their analyses that they had in their hands the silver salt of dibrommaleic acid in a nearly pure condition.

	Calculated		Found by Schmelz and Beilstein.					
	for $Ag_3C_7H_2Br_3O_5$.	for $Ag_2C_4Br_2O_4$.	I.	II.	III.	IV.	V.	VI.
C	11.51	9.84	10.07	10.64	11.30			
H	0.27	—	0.64	0.37	0.32			
Br	32.87	32.78				32.47		
Ag	44.38	44.27					44.25	44.26

With this close agreement between the observed and calculated percentages, I did not consider it worth while to analyze, myself, this silver salt. Still it was evidently necessary to prepare from it the barium salt in order to compare this with the product I had already studied.

Since argentic bromide is readily formed when the silver salt of mucobromic acid is heated with water, I added at once an excess of argentic oxide to a warm solution of mucobromic acid, and heated it quickly to the boiling point. The oxidation seemed to be more neatly accomplished in this way than by the gradual addition of the argentic oxide, although even then there was formed a considerable quantity of argentic bromide. After the action had ceased, the whole was acidified with hydrochloric acid, and the filtered solution shaken out with ether. The acid left upon evaporation of the ether was then taken up with water, neutralized with baric carbonate, and the barium salt purified as before. An analysis of the air-dried salt, and a determination of its solubility, proved that the acid was identical with that made by the action of bromine upon succinic or mucobromic acid.

0.5225 grm. of the air-dried salt gave 0.2741 grm. $BaSO_4$.

Calculated for $BaC_4Br_2O_4.2H_2O$.		Found.
Ba	30.78	30.84

9.2092 grm. of an aqueous solution saturated at 18°.5 according to the method of V. Meyer, gave on evaporation with H_2SO_4 and ignition 0.2944 grm. $BaSO_4$.

According to this determination, an aqueous solution saturated at 18°.5 contains 5.61 per cent of the anhydrous salt.

This oxidation of mucobromic acid by means of argentic oxide into dibrommaleic acid,

$$C_4H_2Br_2O_3 + O = C_4H_2Br_2O_4,$$

would seem to show conclusively that it is the half aldehyde of the dibasic dibrommaleic acid.

Decomposition by Heat.

If mucobromic acid is quickly heated, the greater part of it distils unchanged; but, if the temperature is so regulated that it can distil but slowly, a great part of it suffers decomposition. The reaction which it undergoes I have, as yet, studied only so far as to prove that dibrommaleic acid is one of the chief products. If the acid is mixed with sand and slowly distilled, streams of hydrobromic acid and carbonic dioxide are given off, and a colorless oil passes over, which, on standing, partially solidifies. On the addition of water, the solid portion dissolves, leaving an oil which is volatile with steam, and is not wholly insoluble in water. Its aqueous solution reduces argentic oxide, and possesses an intolerably sharp, pungent odor. In the investigation of this oil, I have not yet obtained definite results.

The aqueous solution contained dibrommaleic acid, which was identified by an analysis of its barium salt. The solution of the barium salt obtained, at first was highly colored, and from it pure material could be made only by repeated precipitation from aqueous solution with the smallest possible quantity of alcohol. In this way, a perfectly colorless salt was made, and it was then recrystallized from water.

0.6652 grm. of the air-dried salt gave 0.3498 grm. $BaSO_4$.

	Calculated for $BaC_4Br_2O_4 . 2H_2O$.	Found.
Ba	30.78	30.91

The amount of dibrommaleic acid thus formed is about 15 per cent of the mucobromic acid taken, and 30 per cent of the total weight of the distillate.

Action of Baric Hydrate.

The action of baric hydrate upon mucobromic acid was first studied by Schmelz and Beilstein. The results they obtained were extremely interesting, but needed extension in several directions. More especially inviting was the muconic acid which they considered formed in the reaction, and to which they gave the formula $H_2C_4O_8$. In beginning this investigation, Mr. O. R. Jackson and I thought it best at the outset to test experimentally the truth of the equation,

$$2C_4H_2Br_2O_3 + H_2O = C_4H_2O_8 + C_2HBr + 2CO_2 + 3HBr,$$

which Schmelz and Beilstein had given as an expression of the reaction, and at the same time to determine the conditions most favorable to the formation of baric muconate. The qualitative results we found to be precisely in accordance with their statements, and it was only necessary to study the reaction quantitatively. A weighed quantity of mucobromic acid was introduced into a flask fitted with reverse cooler, and dissolved in a little warm water. The upper end of the cooler was then connected with a series of wash-bottles which were filled with an ammoniacal solution of cuprous oxide, made by reducing an ammoniacal solution of pure cupric sulphate with metallic copper. The air in the apparatus was then displaced by pure hydrogen, a measured quantity of a standard solution of baric hydrate introduced into the flask, and heat applied. When the action appeared to be finished, we determined the weight of the baric carbonate which had been formed in the reaction, the weight of the baric carbonate which could be precipitated from the filtered solution by carbonic dioxide, and the weight of the baric muconate left on evaporation after washing out the baric bromide with cold water. In order to determine the amount of bromacetylen, we filtered off the voluminous precipitate of acetylen copper which had separated in the wash-bottles, acidified the filtrate, and precipitated the bromine with argentic nitrate.

The results which we obtained are given in the following table; in each case 2 grm. of mucobromic acid were taken.

No	BaO_2H_2 taken.	$BaCO_3$ by CO_2.	Br.	$BaCO_3$ formed.	"Baric muconate."
I.	1.994		0.372	0.57	
V.	2.971	trace	0.293	1.07	0.40
VI.	2.971	trace	0.333	1.05	0.55
II.	5.988	3.52	0.135	0.54	0.85
III.	5.942	3.25	0.146	0.50	0.87
IV.	5.942	3.40	0.128	0.53	0.97
VII.	8.044	5.75	0.135	0.47	0.95
VIII.	8.044	5.90	0.112	0.35	0.90

In order to compare these results more conveniently, we calculated from them the corresponding molecular ratios.

The following table contains the number of molecules of baric hydrate which we used in the various experiments for the decomposition of one molecule of mucobromic acid, the number of molecules of baric hydrate which actually entered into the reaction, and the fractions of a molecule of bromacetylen, carbonic dioxide, and baric muconate which were formed in each case. In accordance with the results which we afterwards obtained, the muconate is here calculated as baric malonate.

No.	Baric hydrate.		Bromacetylen.	Carbonic dioxide.	"Baric muconate."
	taken.	used.			
I.	1.50	1.50	0.60	0.37	
V.	2.24	2.24	0.47	0.70	0.20
VI.	2.24	2.24	0.54	0.69	0.28
II.	4.51	2.21	0.22	0.35	0.43
III.	4.48	2.35	0.24	0.33	0.44
IV.	4.48	2.25	0.21	0.35	0.49
VII.	6.07	2.30	0.22	0.31	0.48
VIII.	6.07	2.17	0.18	0.23	0.45

These results were sufficient to show that, in the decomposition by baric hydrate, we had to deal with at least two independent reactions; that one of these reactions led to the formation of carbonic dioxide and bromacetylen, while the second had for its chief product the sparingly soluble barium salt, — the baric muconate of Schmelz and Beilstein. Moreover, it was evident that, in order to obtain the best yield of the latter salt, a large excess of baric hydrate should be employed.

In the preparation of the sparingly soluble barium salt, we used five or six molecules of baric hydrate to one of mucobromic acid. When the reaction appeared at an end, we precipitated the excess of baric hydrate with carbonic dioxide, and evaporated the filtered solution to a small volume. When this solution was slowly evaporated upon the water bath, we found, in accordance with the statements of Schmelz and Beilstein, that the salt separated in thin crusts which had no visible crystalline structure. If, however, the solution was boiled down rapidly over the lamp, at a certain point the salt suddenly separated in fine, silky needles, which were still further increased as the solution cooled. These crystals were well washed with cold water, redissolved in boiling water, and precipitated with plumbic acetate. In this way a granular lead salt was thrown down, which, when examined under the microscope, was seen to consist of well-formed rhombic plates. For analysis, the salt was dried at 110°.

I. 0.5939 grm. substance gave 0.2434 grm. CO_2 and 0.0470 grm. of H_2O.
II. 0.3459 grm. gave, by ignition with H_2SO_4, 0.3402 grm. $PbSO_4$.

	Calculated for PbC_4O_3.	Calculated for $PbC_3H_2O_4$.	Found.	
			I.	II.
C	15.84	11.65	11.18	
H	——	0.65	0.88	
Pb	68.32	66.99		67.22

It will be seen that the percentages found correspond closely with those required by plumbic malonate, and differ widely from those required by the formula of Schmelz and Beilstein.

The barium salt also agrees well with the description of baric malonate given by Heintzel[*] and Finkelstein.[†] The analyses we have made of the salt have given us too high a percentage of barium, although materially lower than that found by Schmelz and Beilstein.

I. 0.5212 grm. of the salt, dried at 120°, gave 0.5214 grm. $BaSO_4$.
II. 0.3455 grm. of the salt, dried at 100°, gave 0.3159 grm. $BaSO_4$.
III. 0.2139 grm. of the salt, dried at 100°, gave 0.1956 grm. $BaSO_4$.

	Calculated for $BaC_3H_2O_4.H_2O$.	Found.			
		I.	II.	III.	Schmelz and Beilstein
Ba	53.33	54.70	53.75	53.73	56.32

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[*] Ann. Chem. u. Pharm., cxxix. 133.
[†] Ann. Chem. u. Pharm., cxxxiii. 343.

The result of Schmelz and Beilstein is here calculated for the hydrous salt. They found that the salt, when dried at 100°, lost 4.15 per cent of water at 200°, and contained then 58.6 per cent of barium.

From the lead salt we made the free acid by means of hydric sulphide, and found it very soluble in water or alcohol, less freely in ether. From aqueous solution it crystallized in irregular rhombic plates, occasionally in more compact prismatic forms. After several recrystallizations from water, and thorough drying over sulphuric acid, these crystals melted at 131.5–132°. This agrees with the melting point of malonic acid, as given by Heintzel, although it is somewhat lower than that more recently given by Pinner.* A combustion left no doubt of the identity and the purity of the acid.

0.3849 grm. substance gave 0.4871 grm. CO_2 and 0.1395 grm. H_2O.

	Calculated for $C_3H_4O_4$.	Found.
C	34.61	34.51
H	3.85	4.03

The quantity of baric malonate which we obtained from mucobromic acid agreed with the results of our experiments upon a smaller scale, and amounted to nearly 50 per cent of the theoretical yield. The mother liquors contained, beside baric bromide, baric formiate, whose presence could readily be established by qualitative tests.

Although the gaseous product formed by this decomposition with baric hydrate agreed closely in its qualitative reactions with bromacetylen, it seemed to us advisable to prove its identity a little more rigorously. We therefore passed the gas, diluted with hydrogen, into bromine and water. The crystalline solid which resulted we washed with dilute sodic hydrate, then with water, and finally recrystallized it from alcohol. Thus purified, it formed long, brilliant prisms, which melted at 54°. The melting point of pentabromethan is given by Lennox † as 48°; by Reboul, ‡ 48–50°; by Limpricht and Delbrück, § 50–52°; and by Bourgoin, ‖ 56–57°. The prismatic angle could readily be determined, and the measurement of several individuals gave as its mean value 104° 17′. Reboul gives the same angle in crystals of pentabromethan as 104° 20′, and Bourgoin as 104° 16′.

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* Berichte der deutsch. chem. Gesellsch., viii. 965.

† Lond. R. Soc. Proc., xi. 257; Ann. Chem. u. Pharm., cxxii. 122.

‡ C. R., liv. 1229; Ann. Chem. u. Pharm., cxxiv. 267; Bull. Soc. Chim., 1862, 75.

§ Ann. Chem. u. Pharm., clxv. 297.

‖ Ann. Chim. Phys. [5], iv. 423; Bull. Soc. Chim. [2], xxiii. 175, 257.

The identity of the substance was still further established by analysis.

0.1151 grm. substance gave 0.2547 grm. AgBr.

	Calculated for C_2HBr_5.	Found.
Br	94.12	94.17

After we had proved that malonic acid was one of the final products of the decomposition of mucobromic acid when boiled with an excess of baric hydrate, we attempted, by various modifications of the mode of decomposition, to isolate intermediate products, which might give us information concerning the nature of the reaction. After many unsuccessful experiments, we found that such products resulted from the action of alkalies at ordinary temperatures, and they were most conveniently studied when baric hydrate was employed.

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2$. If mucobromic acid is gradually added to a solution of baric hydrate containing a large excess of baric hydrate in suspension, it dissolves readily, and the crystals of baric hydrate at the same time gradually disappear. After a while a beautifully crystalline barium salt begins to separate, the amount of which increases rapidly as the acid is added. In order to prepare this salt, we found it best to add the mucobromic acid until one molecule had been used for every one and a half molecules of baric hydrate. At first we used two parts of crystallized baric hydrate and four of water to one part of mucobromic acid, but subsequently we reduced the amount of water one half. After the necessary amount of mucobromic acid had been added in small portions, care being taken to prevent any elevation of temperature, the whole was allowed to stand for a short time, and the crystals which had separated were then filtered off on the pump. These were washed with a little cold water, exposed to carbonic dioxide until neutral in their reaction, and then recrystallized from water or diluted alcohol. From alcohol, the salt crystallized in pearly rhombic plates; from water, in irregular leafy forms, or, on slow evaporation, in massive aggregates of rhombic plates. When dried by exposure to the air, they lost nothing over sulphuric acid or when heated to 80°. At 100° they slowly lost in weight.

The air-dried salt gave on analysis the percentages required by the barium salt of a dibromacrylic acid.

I. 1.0621 grm. of the salt gave 0.4745 grm. CO_2 and 0.0780 grm. H_2O.
II. 1.0363 grm. of the salt gave 0.4609 grm. CO_2 and 0.0743 grm. H_2O.
III. 0.6187 grm. gave, on ignition with H_2SO_4, 0.2415 grm. $BaSO_4$
IV. 0.6180 grm. gave 0.2434 grm. $BaSO_4$.
V. 0.5785 grm. gave 0.2269 grm. $BaSO_4$.
VI. 0.3522 grm. gave 0.1381 grm. $BaSO_4$.

Calculated for $Ba(C_3HBr_2O_2)_2$.		Found.					
		I.	II.	III.	IV.	V.	VI.
C	12.10	12.19	12.14				
H	0.34	0.82	0.80				
Ba	23.03			22.95	23.15	23.05	23.05

Argentic Dibromacrylate, $AgC_3HBr_2O_2$. From the barium salt, or, better, from a solution of the free acid, the silver salt was made by the addition of argentic nitrate. It is precipitated in the form of fine, felted needles, even from a dilute solution of the acid; it may be recrystallized from hot water without any essential decomposition, and forms then long, flattened needles. The salt was dried over sulphuric acid for analysis.

I. 0.9755 grm. substance gave 0.3890 grm. of CO_2 and 0.0432 grm. of H_2O.
II. 0.3200 grm. substance gave, by the method of Carius, 0.3545 grm. AgBr.
III. 0.7148 grm. substance, precipitated with HBr, gave 0.4005 grm. AgBr.
IV. 0.3668 grm. gave, with HBr, 0.2056 grm. AgBr.

Calculated for $AgC_3HBr_2O_2$.		Found.			
		I.	II.	III.	IV.
C	10.69	10.87			
H	0.30	0.49			
Br	47.47		47.14		
Ag	32.05			32.18	32.20

Plumbic Dibromacrylate, $Pb(C_3HBr_2O_2)_2$. The lead salt is precipitated in pearly rhombic scales by the addition of plumbic acetate to a solution of the free acid. It is readily soluble in hot water, sparingly in cold. When dried over sulphuric acid *in vacuo*, it gave: —

I. 0.3232 grm. substance gave 0.1289 grm. CO_2 and 0.0230 grm. H_2O.

II. 0.4060 grm. gave 0.1858 grm. $PbSO_4$.

III. 0.4908 grm. gave 0.2230 grm. $PbSO_4$.

Calculated for $Pb(C_3HBr_2O_2)_2$.		Found. I.	II.	III.
C	10.82	10.86		
H	0.30	0.79		
Pb	31.13		31.27	31.05

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3H_2O$. On neutralizing a solution of the acid with calcic carbonate, and concentrating the solution on the water bath, the calcium salt was obtained in clusters of radiating needles, tolerably soluble even in cold water. The salt gradually effloresced over sulphuric acid, and lost its crystal water completely at 80–85°.

0.7342 grm. of the air-dried salt lost, at 80–85°, 0.0695 grm. of H_2O.

Calculated for $Ca(C_3HBr_2O_2)_2 . 3H_2O$.		Found.
H_2O	9.78	9.47

0.4951 grm. of the salt, dried at 80–85°, gave, on ignition with H_2SO_4, 0.1354 grm. $CaSO_4$.

Calculated for $Ca(C_3HBr_2O_2)$.		Found.
Ca	8.03	8.04

Potassic Dibromacrylate, $KC_8HBr_2O_2$. The acid neutralized with potassic carbonate and evaporated gave, on cooling, crystals of the potassium salt. From neutral solutions it crystallizes in transparent, six-sided, clustered plates. If but a small amount of free acid is present, it crystallizes in fine, felted needles. Both forms are anhydrous, and do not lose in weight at 80°.

0.5506 grm. gave, on ignition with H_2SO_4, 0.1792 grm. K_2SO_4.

Calculated for $KC_3HBr_2O_2$.		Found.
K	14.58	14.61

An acid salt much less soluble in water may be made by adding acid to a solution of the potassium salt. It crystallizes in long needles, which are anhydrous. The salt is not particularly stable, and the excess of acid may be washed out with ether. The salt was dried by exposure to the air, after several recrystallizations from hot water.

I. 0.6116 grm. substance gave, on ignition with H_2SO_4, 0.1151 grm. K_2SO_4.

II. 0.5395 grm. of substance gave 0.0959 grm. K_2SO_4.

	Calculated for $KC_3HBr_2O_2 . C_3H_2Br_2O_2$.	Found	
		I.	II.
K	7.85	8.45	7.98

Dibromacrylic Acid. From the pure barium salt we set free the acid by the addition of hydrochloric acid, and extracted it from the solution with ether. The ether left, upon evaporation, a white, crystalline acid, which was very soluble in alcohol, ether, or chloroform, and but sparingly soluble in benzol, carbonic disulphide, or ligroin. Under water, it melted at about 20°, dissolved in every proportion on heating, and was but slowly volatilized with steam. The acid, when melted under water, could be made to crystallize either by cooling with ice or by the addition of a mineral acid. After recrystallization from benzol, it melted at 83–84°, and this melting point we were unable to raise by further recrystallization from this or other solvents.

Although our analyses left no doubt of the formula of the substance, they showed that it was still impure.

I. 1.3074 grm. substance gave 0.7692 grm. CO_2 and 0.1121 grm. H_2O.
II. 0.9833 grm. substance gave 0.5797 grm. CO_2 and 0.0877 grm. H_2O.
III. 0.2042 grm. gave 0.3366 grm. AgBr.
IV. 0.2447 grm. gave 0.4044 grm. AgBr.
V. 0.2083 grm. gave 0.3453 grm. AgBr.
VI. 0.2005 grm. gave 0.3309 grm. AgBr.
VII. 0.2132 grm. gave 0.3517 grm. AgBr.

	Calculated for $C_3H_2Br_2O_2$.	Found.						
		I.	II.	III.	IV.	V.	VI.	VII.
C	15.65	16.04	16.08					
H	0.87	0.95	0.99					
Br	69.56			70.15	70.33	70.53	70.23	70.20

Our results had sufficiently established the fact that a dibromacrylic acid was formed from mucobromic acid by the action of baric hydrate in the cold, but a more extended investigation of it was evidently needed to determine the nature of the impurity which was so difficult of removal. Since Wallach and Reincke* had shortly before announced that they were engaged in making from bromalid a dibromacrylic acid, which we thought probable, although upon very insufficient grounds, would prove to be identical with ours, we felt compelled for the moment to suspend our investigations. The other portions of the research afterward claimed so much attention that no study of the acid has yet been made sufficiently extended to establish the conditions essential to its preparation in a pure state. It has been found, however, that an acid melting at 84–85° contains but a slight excess of bromine (I.), and that the pure acid (II.) melts at 85–86°.

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* Berichte der deutsch. chem. Gesellsch. x. 2128.

I. 0.2204 grm. substance gave 0.3621 grm. AgBr.
II. 0.2650 grm. substance gave 0.4336 grm. AgBr.

Calculated for $C_3H_2Br_2O_2$.		Found. I.	Found. II.
Br	69.56	69.90	69.65

For purposes of comparison, certain determinations of the solubility of the acid and its barium salt may find a place here, although they were not made with absolutely pure material, and are therefore subject to revision. In determining the solubility of the acid, the saturated solution, made according to the method of V. Meyer, was neutralized with baric carbonate, and the dissolved barium determined by precipitation with sulphuric acid.

I. 14.7798 grm. of a solution, saturated at 20°, gave 0.4488 grm. $BaSO_4$.
II. 8.6788 grm. of a solution, saturated at 20°, gave 0.2630 grm. $BaSO_4$.

According to these determinations, an aqueous solution of the acid, saturated at 20°, contains the percentages: —

I.	II.
5.98	5.98

8.4992 grm. of a solution of the barium salt, saturated at 20°, gave, on evaporation with H_2SO_4 and ignition, 0.1912 grm. $BaSO_4$.

The aqueous solution of baric dibromacrylate, saturated at 20°, therefore contains 5.74 per cent of the dry salt.

In studying the behavior of this dibromacrylic acid towards reagents, we have been able to use only the product melting at 83–84°, which may easily be obtained in any quantity desired. When boiled with an excess of baric hydrate, the acid is completely decomposed, baric carbonate is precipitated, bromacetylen set free, and at the same time baric malonate is formed in abundance. For complete identification, the baric malonate was converted into the lead salt, and the latter analyzed.

0.5179 grm. of the salt, dried at 110°, gave, on ignition with H_2SO_4, 0.5062 grm. $PbSO_4$.

Calculated for $PbC_3H_2O_4$.	Found.
66.99	66.79

The amount of baric malonate formed in this decomposition with an excess of baric hydrate was found to be forty-nine per cent of the theoretical yield as the mean of two determinations.

The behavior of the acid towards hydrobromic acid was studied by Mr. C. F. Mabery. It is not altered by ordinary concentrated hydrobromic acid (b. pt. 126°), nor is it affected in the cold by an acid saturated at 0°; but it forms an addition-product when heated with it for several hours at 100°. The reaction is by no means neat, and a large portion of the substance is charred. The tribrompropionic acid which is thus formed differs essentially in its melting-point (116–117°) and other physical properties from the acid melting at 93° mentioned by Linnemann and Penl,* and recently more fully described by Michael and Norton;† and also from the acid melting at 53°, which was obtained by Fittig and Petri,‡ by the action of hydrobromic acid upon their dibromacrylic acid. It is sparingly soluble in cold water, readily in hot, and may be crystallized without difficulty from hot water. It is readily soluble in alcohol or ether, somewhat less soluble in chloroform. From water it crystallizes in pearly scales, which melt at 116–117°. Argentic nitrate precipitates from an aqueous solution of the acid, the silver salt in clustered rhombic plates.

0.1892 grm. of the acid gave 0.3453 grm. AgBr.

	Calculated for $C_3H_3Br_3O_2$.	Found.
Br	77.16	77.64

If one molecule of bromine is added to dibromacrylic acid dissolved in chloroform, the color of the bromine gradually disappears, and after the lapse of some time tetrabrompropionic acid separates in large, well-formed crystals, which melt at 125°. This acid is at present under investigation in this laboratory.

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* Berichte der deutsch. chem. Gesellsch., viii. 1098.

† Amer. Chem. Journ., ii. 18.

‡ Ann. Chem. u. Pharm., cxcv. 73.

One well-marked product of the decomposition of mucobromic acid by cold baric hydrate had been shown to be baric dibromacrylate; it only remained to study the more soluble products of the reaction. In continuing the investigation with Mr. O. R. Jackson, the filtrate from the crystals of baric dibromacrylate was treated with carbonic dioxide to remove the excess of baric hydrate, filtered from the baric carbonate, and the filtrate evaporated at a gentle heat (40–50°). In the course of this evaporation, a certain amount of baric dibromacrylate crystallized out, which was removed from time to time. When the liquid had been reduced to about one third its original volume, it was precipitated by the addition of two volumes of alcohol. The bulky crystalline precipitate thus thrown down proved upon qualitative examination to consist chiefly of baric formiate. When purified by repeated precipitation from aqueous solution by alcohol and recrystallization from water, it showed the characteristic form of baric formiate.

0.3964 grm. substance gave, on ignition with H_2SO_4, 0.4054 grm. $BaSO_4$.

	Calculated for $Ba(CHO_2)_2$.	Found.
Ba	60.36	60.13

The lead salt made from the barium salt crystallized in the characteristic form of plumbic formiate, and gave on analysis the required percentage of lead.

0.4149 grm, of the salt gave, on ignition with H_2SO_4, 0.4221 grm. $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	69.50

In the alcoholic filtrate from the baric formiate, we were able to find, beside baric bromide, only a crystallizable barium salt, well marked by its qualitative reactions, but so unstable that we were not able to effect its purification. The behavior of this salt, and the analyses which we made of it in an impure state, led us to the conclusion that it was the barium salt of brompropiolic acid, formed by subtraction of hydrobromic acid from the dibromacrylic; and this view was subsequently proved to be correct by a study of the addition products which the corresponding acid formed with the halogens and the haloid acids.

Since all our attempts to isolate a pure salt from a solution containing baric bromide had proved unsuccessful, we attempted to take advantage of a remarkably stable molecular compound which the corresponding acid forms with dibromacrylic acid. This compound may readily be made by acidifying the baric hydrate solution of mucobromic acid, without removing the separated baric dibromacrylate, and extracting the solution with ether. The same compound, although in smaller quantity, may also be obtained, after that portion of the barium salt which separates spontaneously is removed. From dibromacrylic acid it may be made by the action of baric hydrate in the cold. For its preparation we usually have employed a solution of potassic, instead of baric, hydrate. The proportions which we have found most advantageous are 70 grm. of potassic hydrate and 400 c.c. of water to 100 grm. of mucobromic acid. Care must be taken in adding the mucobromic acid, and also in the subsequent acidification with hydrochloric acid, that no sensible elevation of temperature takes place. When the solution is partially acidified, the acid potassium salt of dibromacrylic acid usually separates in abundance, but dissolves upon further addition of acid. The solution is then thoroughly extracted with ether; and this leaves on distillation a liquid residue, which, on cooling, gradually solidifies in large, well-formed, monoclinic (?) prisms. These are readily soluble in water, alcohol, ether, or chloroform, and may be purified by crystallization from hot benzol, or more conveniently by melting with a little water. Thus purified, the substance melts at 104–105°; and this melting point is not altered by repeated recrystallizations from various solvents.

I. 0.9023 grm. substance gave 0.6440 grm. CO_2 and 0.0850 grm. H_2O.
II. 0.4403 grm. substance gave 0.3157 grm. CO_2 and 0.0433 grm. H_2O.
III. 0.2263 grm. substance gave 0.3386 grm. AgBr.
IV. 0.2241 grm. substance gave 0.3321 grm. AgBr.
V. 0.2092 grm. substance gave 0.3139 grm. AgBr.

	Calculated for $C_6H_3Br_3O_4$.	Found.				
		I.	II.	III.	IV	V.
C	19.00	19.43	19.54			
H	0.79	1.05	1.09			
Br	63.33			63.66	63.03	63.84

Although the percentages we have found show a considerable variation from those calculated for equal molecules of dibromacrylic and brompropiolic acids, they agree better with this than with any other formula equally simple; and, moreover, the qualitative behavior of the substance is such as to render this formula tolerably certain. Its aqueous solution gives, on the addition of plumbic acetate, an immediate crystalline precipitate of plumbic dibromacrylate.

0.3560 grm. gave, on ignition with H_2SO_4, 0.1628 grm. $PbSO_4$.

	Calculated for $Pb(C_3HBr_2O_2)_2$.	Found.
Pb	31.13	31.25

So also if it is neutralized with baric carbonate, the solution gives, on spontaneous evaporation, crystals of baric dibromacrylate, while in solution remains a much more soluble salt, with all the characters of baric brompropiolate. That this substance contains the brompropiolic acid is shown by the evolution of carbonic dioxide and bromacetylen when its aqueous evolution is boiled.

Starting with this molecular compound melting at 104–105°, we made various attempts to isolate the brompropiolic acid and its salts in a pure state. The barium salts of dibromacrylic and brompropiolic acids showed such marked differences in their solubility in water or in alcohol that we hoped through them to effect a complete separation of the two acids. We found, however, that it was difficult to obtain in this way a colorless salt of brompropiolic acid which appeared even tolerably pure. We therefore attempted to separate the two acids by converting them into their ethyl-ethers and submitting these to fractional distillation. We dissolved the molecular compound (m. pt. 104°) in absolute alcohol, added concentrated sulphuric acid, and warmed. The ethers soon separated in part, and were precipitated with water, washed with dilute sodic carbonate, and dried over fused calcic chloride. These mixed ethers had an extremely sharp, pungent odor, and their vapor attacked the eyes violently. On attempting to separate the two by distillation, we found that a large portion of the liquid was carbonized in each distillation, and that but one volatile product could be isolated. This was a mobile liquid, of an agreeable aromatic odor, which boiled between 209 and 215°, without any very noticeable decomposition. The portion of this which boiled between 212–214° was analyzed, and found to be essentially the ethyl-ether of dibromacrylic acid, although still impure. Since our chief object was to isolate the ether of the brompropiolic acid, and this had evidently been for the most part destroyed, the substance was not farther examined.

0.5235 grm. of substance gave, on combustion, 0.4675 grm. CO_2 and 0.1250 grm. H_2O.

	Calculated for $C_3HBr_2O_2 . C_2H_5$.	Found.
C	23.23	24.36
H	2.33	2.65

Finally, we attempted to separate the two acids by fractional saturation. Although the products thus obtained gave us analytical results that were far from satisfactory, we found that the separation could be effected with tolerable precision, the brompropiolic acid being the stronger acid, and that this was the most convenient way of preparing material sufficiently pure for further work, in any considerable quantity. Pure substance melting at 104–105° was dissolved in water, and a little less than the calculated amount of baric carbonate was added. The clear solution was then freed as completely as possible from dibromacrylic acid by repeated extraction with ether, and the baric brompropiolate obtained by spontaneous evaporation.

Our analytical results show that the material analyzed was not pure, and yet they leave no doubt as to its nature.

I. 0.6974 grm. of substance, dried over H_2SO_4, gave 0.3968 grm. CO_2 and 0.0347 grm. H_2O.

II. 0.3060 grm. of substance, dried over H_2SO_4, gave 0.1657 grm. $BaSO_4$.

III. 0.1829 grm. of substance, dried over H_2SO_4, gave 0.0973 grm. $BaSO_4$.

IV. 0.4325 grm. of substance, dried over H_2SO_4, gave 0.2305 grm. $BaSO_4$.

	Calculated for $Ba(C_3BrO_2)_2$.	Found.			
		I.	II.	III.	IV.
C	16.63	15.52			
H	—	0.55			
Ba	31.63		31.84	31.27	31.32

We have been unable to make any satisfactory determinations of the water of crystallization, since the salt cannot be heated, and even on standing over sulphuric acid in the cold it is slowly decomposed. The salt when crystallized from water probably contains four molecules of water.

I. 2.1104 grm. of the air-dried salt lost over sulphuric acid 0.2803 grm.

II. 0.9828 grm. of air-dried substance lost over H_2SO_4 0.1316 grm.

	Calculated for $Ba(C_3BrO_2)_2.4H_2O$	Found.	
		I.	II.
H_2O	14.26	13.28	13.39

In one instance the salt precipitated from alcoholic solution by the addition of ether was found to contain but a single molecule of water.

1.0639 grm. of air-dried salt lost over H_2SO_4 *in vacuo* 0.0458 grm.

	Calculated for $Ba(C_3BrO_2)_2.H_2O$.	Found.
H_2O	3.99	4.30

The salt usually crystallized, on the slow evaporation of its aqueous solution, in small, oblique prisms; but it sometimes separated, on long standing, in more compact, clustered, rhombic plates. When dry, it is decomposed quite rapidly at 50°, and deflagrates at about 125°. In aqueous solution it is recomposed on boiling, with the precipitation of baric carbonate and the evolution of carbonic dioxide and bromacetylen. From solutions containing an excess of the acid, a somewhat more stable salt separates in fine, felted needles, less soluble in water than the neutral salt. This would seem to be an acid salt, corresponding to the acid potassium salt of dibromacrylic acid; but we could obtain no satisfactory analytical results.

When argentic nitrate is added to a solution of the barium salt, or of the free acid, a white, amorphous silver salt is precipitated, and at the same time if the solution is concentrated the evolution of carbonic dioxide is noticed. The precipitate turns yellow on washing, and is evidently still further decomposed on drying. When gently warmed with water, it is slowly decomposed; but, when suddenly heated nearly to 100°, it explodes violently, with the separation of large quantities of carbon. In a dry state it explodes when heated to about 75°. In dilute nitric acid it dissolves at first; but the solution soon grows turbid, smells strongly of bromacetylen, and argentic bromide is precipitated. One could hardly expect trustworthy results from the analysis of so unstable a substance. One silver determination, however, showed that it must be considered a derivative of bromacetylen, rather than of brompropiolic acid.

0.2313 grm. of substance, dried over H_2SO_4 *in vacuo*, gave 0.1975 grm. AgBr.

	Calculated for AgC_3BrO_2;	for AgC_2Br.	Found.
Ag	42.19	50.94	49.05

Although the barium salt had given unsatisfactory results on analysis, we made from it the acid, and hoped then to be able to effect its purification. We therefore precipitated the barium from a cold, aqueous solution, with a slight excess of sulphuric acid, and extracted the acid from the filtered solution with ether. We obtained in this way long, slender prisms, extremely soluble in water, alcohol, or ether, readily in chloroform or benzol, more sparingly in carbonic disulphide, and but slightly soluble in ligroin. The crystals obtained from aqueous solution by spontaneous evaporation appeared to contain water of crystallization. When pressed with paper they melted at 60–65°; but over sulphuric acid they soon became opaque, and the melting point had risen to 80° or over.

We attempted the purification of the acid by repeated recrystallization from ligroin to which a little ether had been added. The long, silky needles thus obtained melted at 86°, but gave on analysis no satisfactory results (I. and II.). Although the acid was blackened and apparently completely decomposed at a temperature but little over 100°, we found that it could be sublimed readily between watch-glasses at steam heat. The melting point was, however, lowered rather than raised, by successive sublimations, and analyses (III. and IV.) of the sublimed product gave too high a percentage of bromine.

I. 0.3010 grm. substance gave 0.4025 grm. AgBr.
II. 0.1198 grm. substance gave 0.1582 grm. AgBr.
III. 0.2010 grm. substance gave 0.2580 grm. AgBr.
IV. 0.1820 grm. substance gave 0.2339 grm. AgBr.

	Calculated for C_3HBrO_2.	Found.			
		I.	II.	III.	IV.
Br	53.69	56.90	56.21	54.63	54.69

The acid is decomposed, with the formation of carbonic dioxide and bromacetylen, on boiling its aqueous solution. When heated with an excess of baric hydrate, baric carbonate is precipitated, bromacetylen is evolved, and at the same time baric malonate is formed in abundance. It unites with dibromacrylic acid immediately to form the characteristic addition-product. An ethereal solution containing a mixture of the two acids, approximately in molecular proportions, gave on evaporation a substance which, without purification, melted at 103°. With the halogens and haloid acids, it forms addition-products with the greatest readiness. The substituted acrylic acids which are thus formed, according to the equations, —

$$C_3HBrO_2 + HX = C_3H_2BrXO_2$$
$$C_3HBrO_2 + X_2 = C_3HBrX_2O_2,$$

are easily purified, and their formation can leave no doubt of the nature of the brompropiolic acid. Several of these acids will be described later in this paper.

The decomposition of mucobromic acid by baric hydrate, under the conditions described, may be expressed by the following equations. The first action would seem to be the assimilation of a molecule of water and the formation of dibromacrylic and formic acids.

$$C_4H_2Br_2O_3 + H_2O = C_3H_2Br_2O_2 + CH_2O_2$$

This action is immediately followed, even in the cold, by the subtraction of hydrobromic acid, —

$$C_3H_2Br_2O_2 - HBr = C_3HBrO_2$$

The brompropiolic acid is then either decomposed by heat, —

$$C_3HBrO_2 = C_2HBr + CO_2,$$

or is converted into malonic acid, —

$$C_3HBrO_2 + 2H_2O = C_3H_4O_4 + HBr$$

Since a large percentage of dibromacrylic acid was converted into brompropiolic acid in this reaction, and it had previously been proved that a portion of the mucobromic acid entirely escaped decomposition when the proportion of baric hydrate was materially lessened, I recently attempted to increase the yield by reversing the mode of procedure. I therefore added baric hydrate, gradually, to mucobromic acid suspended in a little water; taking care, after the acid was neutralized, to make the solution but slightly alkaline, and to wait until it was again neutral before further addition. I found, however, that an entirely different reaction had taken place under these conditions, and that among the products of this reaction little or no dibromacrylic acid could be found. This decomposition is at present under investigation in this laboratory, and all discussion of the results we have already obtained must therefore be reserved for a subsequent paper.

MUCOCHLORIC ACID.

Mucochloric acid was discovered in 1865 by Schmelz and Beilstein,* and since that time, as far as I know, it has never been further studied. The discoverers found its preparation so very laborious, and the yield which they obtained so small, that they made no extended investigation of it, but contented themselves with giving a short description of the acid, together with the analyses necessary to establish its composition. Although their account was certainly not encouraging, it seemed to me worth while to attempt its preparation, more especially in order to study the dichloracrylic acid derived from it, and to compare this with the acid of the same composition which Wallach* had already made from chloralid. This investigation Mr. W. Z. Bennett undertook with me.

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* Ann. Chem. u. Pharm., Suppl., iii. 280.

The method followed by Schmelz and Beilstein in making mucochloric acid was as follows: Pyromucic acid suspended in water was treated with chlorine at first in the cold and afterwards at boiling heat. When all action appeared to be over, the solution was somewhat concentrated on the water bath, and finally brought to crystallization by evaporation over sulphuric acid *in vacuo.* This method gave in our hands precisely the same discouraging quantitative results that Schmelz and Beilstein had obtained; and it was only after a long series of unsuccessful experiments that we succeeded in finding a simple modification of the method which enabled us to prepare material sufficient for investigation. We suspended the pyromucic acid in ten times its weight of water, cooled the whole well with ice, and passed in a rapid stream of chlorine until the liquid was thoroughly saturated. The temperature was carefully kept within a few degrees of the freezing point during this treatment with chlorine, and not unfrequently considerable quantities of the crystalline hydrate of chlorine separated. When the solution was saturated it was heated to boiling, after a few moments again cooled to 0°, and saturated once more with chlorine. When this operation had been repeated several times, crystals of mucochloric acid began to appear as the solution cooled. At first we filtered these crystals off, and subjected the filtrate to further treatment; but we found by experience that little or no product was gained after the sixth chlorination, and we, therefore, usually proceeded to this point before we removed the acid formed. We then collected the crystals which separated as the solution cooled, and evaporated the mother liquors on the water bath to the point of crystallization. The crystals were drained, pressed, and recrystallized from hot water. We further found it convenient to add to the pyromucic acid a small percentage of iodine. Although this was by no means essential, we found that our results were then more constant and the average yield greater. As the result of several preparations which we made in the course of the investigation, we obtained 129 grm. of mucochloric acid from 202 grm. of pyromucic acid. This corresponds to a little more than forty per cent of the theoretical amount, as our average product, although in single instances our yield has reached 50 per cent. The product made in this way crystallized from water in well-formed rhombic plates, which in their properties agreed in every particular with the description of Schmelz and Beilstein. The acid melted at 125°, and was very soluble in alcohol or ether, sparingly soluble in cold water, readily in hot. Boiling benzol or chloroform dissolved it with readiness, while in carbonic disulphide or ligroin it was almost insoluble. The purity of our material was shown by the following analyses: —

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* Berichte der deutsch. chem. Gesellsch., viii. 1580.

I. 0.7408 grm. substance gave 0.7617 grm. CO_2 and 0.0831 grm. H_2O.
II. 0.5512 grm. substance gave 0.5687 grm. CO_2 and 0.0621 grm. H_2O.
III. 0.2090 grm. substance gave 0.3564 grm. AgCl.

Calculated for $C_4H_2Cl_2O_3$.			Found.	
		I.	II.	III.
C	28.40	28.06	28.13	
H	1.18	1.25	1.25	
Cl	42.01			42.16

Although mucochloric acid appears to form derivatives in some respects more stable and readily studied than the corresponding derivatives of mucobromic acid, we have thus far taken up more in detail only the dichloracrylic acid which may easily be made from it by the action of alkalies.

Dichloracrylic Acid.

In 1877, Wallach[*] obtained a dichloracrylic acid as a product of the reduction of chloralid. This acid was afterward more carefully studied by Wallach and Hunäus,[†] and quite recently Wallach[‡] has published a paper still further describing the acid and its salts, and correcting the work of Hunäus in several important particulars. At the time this investigation was begun, this acid was the only disubstituted acrylic acid known, and since its constitution was fairly established by the mode of its preparation, it seemed desirable to prepare the dichloracrylic acid from mucochloric, in order to compare the two acids.

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[*] Berichte der deutsch. chem. Gesellsch., viii. 1580.

[†] Berichte der deutsch. chem. Gesellsch., x. 567. Ann. Chem. u. Pharm. cxciii. 19.

[‡] Ann. Chem. u. Pharm. cciii. 83.

The decomposition of mucochloric acid into dichloracrylic and formic acids, under the influence of alkalies, is much more neatly accomplished than the corresponding reaction with mucobromic acid. Under ordinary conditions, but little hydrochloric acid is split off, and the yield of dichloracrylic acid is nearly 90 per cent of that required by the equation, —

$$C_4H_2Cl_2O_3 + H_2O = C_3H_2Cl_2O_2 + CH_2O_2.$$

We never have noticed in the preparation of dichloracrylic acid either chlorpropiolic acid or any compound corresponding to that which brompropiolic acid forms with dibromacrylic. We usually have dissolved mucochloric acid in quite an excess of potassic hydrate, allowed the solution to stand for a short time, acidified with hydrochloric acid, and extracted with ether. The dichloracrylic acid left on evaporation of the ether may be purified by melting it several times with a little water. When dried over sulphuric acid it gave the following results on analysis: —

I. 0.5280 grm. substance gave 0.4894 grm. CO_2 and 0.0720 grm. H_2O.
II. 0.3670 grm. substance gave 0.3399 grm. CO_2 and 0.0477 grm. H_2O.
III. 0.1037 grm. substance gave 0.2123 grm. AgCl.
IV. 0.2674 grm. substance gave 0.5420 grm. AgCl.

	Calculated for $C_3H_2Cl_2O_2$.	Found.			
		I.	II.	III.	IV.
C	25.54	25.28	25.25		
H	1.42	1.51	1.45		
Cl	50.36			50.62	50.10

This dichloracrylic acid forms small rhombic prisms which volatilize rapidly on exposure to the air. It is readily soluble in water, alcohol, ether, or chloroform, and it also dissolves freely in boiling benzol, carbonic disulphide, or ligroin. It melts at 85–86°, and, when solidified by quick cooling, melts again at the same temperature. The β dichloracrylic acid of Wallach, on the other hand, melts at 76–77° and its melting point falls to 63–64° when melted and suddenly cooled.

Argentic Dichloracrylate, $AgC_8HCl_2O_2$. The silver salt was precipitated in the form of fine felted needles on the addition of argentic nitrate even to a dilute solution of the acid. The salt was quite stable and could be recrystallized from hot water without any marked decomposition.

I. 0.5460 grm. substance gave 0.2808 grm. CO_2 and 0.0299 grm. H_2O.
II. 0.4819 grm. substance gave 0.2494 grm. CO_2 and 0.0253 grm. H_2O.
III. 0.2511 grm. substance gave, by Cairus' method, 0.2910 grm. AgCl.
IV. 0.2078 grm. substance gave, by Cairus' method, 0.2401 grm. AgCl.
V. 0.2089 grm. substance, precipitated by HCl, gave 0.1209 grm. AgCl.
VI. 0.6768 grm. substance, precipitated by HCl, gave 0.3909 grm. AgCl.

Calculated for $AgC_3HCl_2O_2$.		Found.					
		I.	II.	III.	IV.	V.	VI.
C	14.52	14.03	14.12				
H	0.40	0.60	0.58				
Cl	28.63			28.65	28.56		
Ag	43.54					43.55	43.49

Baric Dichloracrylate, $Ba(C_3HCl_2O_2)_2 . H_2O$. The barium salt was prepared by neutralizing the aqueous solution of the acid with baric carbonate and concentrating the solution upon the water bath. On cooling, the salt separated in rhombic plates which were permanent in the air, and did not lose in weight over sulphuric acid *in vacuo.*

I. 0.2185 grm. of the salt lost, when heated to 80°, 0.0088 grm H_2O and gave, on ignition with H_2SO_4, 0.1174 grm. $BaSO_4$.
II. 0.1941 grm. of the salt gave, on ignition with H_2SO_4, 0.1041 grm. $BaSO_4$.
III. 0.2402 grm. of the salt gave, on ignition with H_2SO_4, 0.1281 grm. $BaSO_4$.
IV. 0.9167 of the salt lost, when heated to 80°, 0.0395 grm. H_2O.

Calculated for $Ba(C_3HCl_2O_2)_2.H_2O$.		Found.			
		I.	II.	III.	IV.
Ba	31.49	31.59	31.53	31.36	
H_2O	4.14	4.03			4.31

For the further characterization of this salt we determined its solubility in cold water by the method of V. Meyer.

I. 5.6625 grm. of an aqueous solution, saturated at 18°, gave, on evaporation and ignition with H_2SO_4, 0.1956 grm. $BaSO_4$.
II. 2.416 grm. of a solution, saturated at 18°.5, gave 0.0801 grm. $BaSO_4$.

These determinations give as the percentages of the anhydrous salt contained in the hot solutions saturated at 18° and 18°.5 respectively

I.	II.
6.28	6.19

Calcic Dichloracrylate, $Ca(C_3HCl_2O_2)_2.3H_2O$. The calcium salt, which was extremely soluble in water, was made by neutralizing a solution of the acid with calcic carbonate. On cooling the concentrated solution, the salt separated in long, flat radiating needles, which were permanent in the air, but slowly effloresced over sulphuric acid.

I. 0.4077 grm. of the air-dried salt lost, on heating to 95–100°, 0.0580 grm. H_2O, and gave, on ignition with H_2SO_4, 0.1488 grm. $CaSO_4$.

II. 0.6163 grm. of the air-dried salt lost, on heating, 0.0875 grm. H_2O.

III. 0.3217 grm. of the dried salt (II.), corresponding to 0.3749 grm. of the air-dried salt, gave, on ignition with H_2SO_4, 0.1348 grm. $CaSO_4$.

Calculated for $Ca(C_3HCl_2O_2)_2.3H_2O$.		Found.		
		I.	II.	III.
Ca	10.69	10.73		10.58
H_2O	14.43	14.23	14.20	

Potassic Dichloracrylate, $KC_3HCl_2O_2$. The potassium salt crystallizes from a solution of mucochloric acid in an excess of potassic hydrate (1 : 4) when this is strongly cooled. Although it is quite soluble even in cold water, it may readily be purified by recrystallization from hot water. From concentrated solutions it crystallizes on cooling in long, slender needles, which are anhydrous.

I. 0.3054 grm. of the salt gave, on ignition and evaporation with HCl, 0.1283 grm. KCl.

II. 0.2159 grm. of the salt gave 0.0908 grm. KCl.

Calculated for $KC_3HCl_2O_2$.		Found.	
		I.	II.
K	21.84	22.03	22.06

The foregoing results seemed to us to show with sufficient precision that our acid was essentially different from the β dichloracrylic acid of Wallach, since the two acids differed markedly in their physical properties, and their salts were also quite dissimilar. Following the analyses of Hunäus, Wallach* had assigned to the barium salt of the β dichloracrylic acid the formula $Ba(C_8HCl_2O_2)_2 \, . \, 5H_2O$, and to the calcium salt the probable formula $Ca(C_3HCl_2O_2) \, . \, 1\frac{1}{2}H_2O$; while the corresponding salts of our acid we had found to have the formulæ $Ba(C_8HCl_2O_2)_2 \, . \, H_2O$ and $Ca(C_3HClO_2)_2 \, . \, 3H_2O$. Although the potassium salt of neither acid contained water of crystallization, one crystallized in plates, the other in needles.

Quite recently Wallach† has published the results of several determinations made since the publication of a preliminary notice ‡ of our dichloracrylic acid. These determinations show that the formulæ which had previously been assigned to the barium and calcium salts of his acid were incorrect, and that they probably each contained two molecules of water. To these determinations, however, Wallach would attach but little weight for the identification of the acid, although he considers the isomerism of the two dichloracrylic acids to be fully established.

"Ich möchte aber nach den gemachten Erfahrungen diesen Bestimmungen vorläufig keinen besonderen Werth für die *Charakterisirung* der Dichloracrylsäure aus Chloralid beilegen. Man wird besser thun, sich dafür an die scharf bestimmbaren Eigenschaften der *gemessenen freien* Säure und allenfalls an die tafelförmige Ausbildung des wasserfreien Kalisalzes, sowie an die angegebenen krystallographischen Daten des Baryumsalzes, anstatt an die bisher ausgeführten Wasserbestimmungen zu halten; für letztere müssen noch weitere Versuche vorbehalten bleiben. Jedenfalls muss aber der Zweck der obigen Angaben jetzt schon als erreicht bezeichnet werden: nämlich die völlige *Verschiedenheit der Dichloracrylsäure aus Chloralid* der nur die Formel $CCl_2 = CH\text{–}CO_2H$ zukommen kann, *von der*, welche Bennett und Hill *aus Mucochlorsäure erhielten definitiv zu bestätigen.*" §

Unfortunately we have as yet been unable to obtain either our acid or its barium salt in a form which would admit of crystallographic study. Still, the differences already established leave no reasonable doubt that the two acids are isomeric, and the acid from mucochloric acid may therefore be distinguished for convenience as the α dichloracrylic acid.

The behavior of this acid towards reagents has thus far been little examined. On boiling with an excess of baric hydrate, it is decomposed in essentially the same way as the dibromacrylic acid, baric malonate being formed in abundance. This decomposition with alkalies we have not followed further, since it was evident that chlorpropiolic acid should be the intermediate product formed; and we wished not to interfere with the researches which Wallach had already undertaken with Bischof,* concerning the decomposition of β dichloracrylic acid by alkalies.

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* Ann. Chem. u. Pharm., cxciii. 23.

† Ibid., cciii. 83.

‡ Berichte der deutsch. chem. Gesellsch., xii. 655.

§ *Loc. cit.*, p. 86.

Although the acid does not add bromine when heated with it to 100° in chloroform solution, it readily forms an addition product when heated for some time with undiluted bromine at 100°. The dichlordibrompropionic acid which is thus formed is at present under investigation in this laboratory.

SUBSTITUTED ACRYLIC ACIDS FROM BROMPROPIOLIC ACID.

Mr. C. F. Mabery has studied with me some of the substituted acrylic acids which may readily be made by the addition of halogens or haloid acids to brompropiolic acid.

Dibromacrylic Acid of Fittig and Petri.

Brompropiolic acid dissolves easily in concentrated hydrobromic acid (b. pt. 126°), and on standing for a short time the solution deposits abundant crystals of a dibromacrylic acid, which is identical with that described by Fittig and Petri as resulting from the decomposition of tribromsuccinic acid. This acid may also be prepared to advantage from the solution of baric brompropiolate and baric bromide which is obtained in the preparation of baric dibromacrylate by the action of baric hydrate upon mucobromic acid. It is only necessary to precipitate the barium with dilute sulphuric acid, and to concentrate the solution upon the water bath. The acid which separates as the solution cools is easily purified by recrystallization.

From a hot concentrated solution, the acid falls at first as an oil; but, after the solution has cooled somewhat, it separates in pearly scales, which melt at 85–86°. In analysis they gave the required percentage of bromine.

0.2614 grm. of substance gave 0.4283 grm. AgBr.

	Calculated for $C_3H_2Br_2O_2$.	Found.
Br	69.57	69.72

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* Berichte der deutsch. chem. Gesellsch., xi. 751; xii. 57.

The solubility of the acid in water at ordinary temperatures we determined by neutralizing with baric carbonate the solution made according to V. Meyer's method, and evaporating the filtered solution with sulphuric acid.

I. 12.5364 grm. of a solution, saturated at 20°, gave 0.2070 grm. $BaSO_4$.
II. 11.6241 grm. of a solution, saturated at 20°, gave 0.1712 grm. $BaSO_4$.
III. 8.4358 grm. of a solution, saturated at 20°, gave 0.1248 grm. $BaSO_4$.
IV. 10.6740 grm. of a solution, saturated at 20°, gave 0.1581 grm. $BaSO_4$.

As the result of these determinations, we find that an aqueous solution of the acid saturated at 20° contains the following percentages: —

I.	II.	III.	IV.
3.16	2.91	2.92	2.93

Fittig and Petri found that the dibromacrylic acid made from tribromsuccinic gave at 20° a solution which contained 3.355 per cent of the acid.

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.2H_2O$. An aqueous solution of the acid was neutralized with baric carbonate, and the filtered solution evaporated on the water bath. On cooling, the barium salt crystallized in rectangular plates, whose angles were, however, often more or less modified.

The air-dried salt lost, on heating to 100°, two molecules of water.

I. 0.4018 grm. of air-dried salt lost at 100° 0.0226 grm. H_2O.
II. 0.4644 grm. of air-dried salt lost at 100° 0.0261 grm. H_2O.
III. 0.5086 grm. of air-dried salt lost at 100° 0.0299 grm. H_2O.

Calculated for $Ba(C_3HBr_2O_2)_2.2H_2O$.		Found.		
		I.	II.	III.
H_2O	5.71	5.62	5.62	5.88

The anhydrous salt then gave: —

I. 0.3425 grm. of substance, dried at 100°, gave on ignition 0.1353 grm. $BaSO_4$.
II. 0.4383 grm. of the salt, dried at 100°, gave 0.1723 grm. $BaSO_4$.
III. 0.2934 grm. of the salt, dried at 100°, gave 0.1153 grm. $BaSO_4$.

Calculated for $Ba(C_3HBr_2O_2)_2$.		Found.		
		I.	II.	III.
Ba	23.03	23.23	23.11	23.10

Fittig and Petri found in two determinations of water, in the barium salt of their acid, a somewhat higher percentage (6.73 and 7.27), and therefore assign it the formula $Ba(C_3HBr_2O_2)_2.2\frac{1}{2}H_2O$ — (calculated 7.03 per cent).

The solubility of the salt we determined by V. Meyer's method.

I. 3.9749 grm. of a solution, saturated at 23°, gave, on evaporation with H_2SO_4 and ignition, 0.1748 grm. $BaSO_4$.

II. 3.9148 grm. of a solution, saturated, at 20°, gave 0.1719 grm. $BaSO_4$.

According to these determinations, the aqueous solution saturated at 20° contained the following percentages of the anhydrous salt: —

I.	II.
11.23	11.21

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3\frac{1}{2}H_2O$. The calcium salt we prepared by neutralizing a solution of the acid with calcic carbonate. On cooling the concentrated solution, the salt separated in long radiating needles.

I. 0.5625 grm. of the air-dried salt lost, when heated to 100°, 0.0668 grm. H_2O, and gave, when ignited with H_2SO_4, 0.1356 grm. $CaSO_4$.

II. 0.3460 grm. of the salt lost at 100° 0.0394 grm. H_2O and gave 0.0850 grm. $CaSO_4$.

	Calculated for $Ca(C_3HBr_2O_2)_2.3\frac{1}{2}H_2O$.	Found.	
		I.	II.
Ca	7.13	7.09	7.22
H_2O	11.23	11.88	11.39

Fittig and Petri found in two determinations of water, in the calcium salt of their acid, the percentages 11.56 and 11.47, from which they calculate the formula with 3½ molecules of water given above.

The physical properties of the acid, and the analyses of the barium and calcium salts, leave no doubt of the identity of this dibromacrylic acid with that described by Fittig and Petri, although our results differ slightly in some respects from theirs. The acid from tribromsuccinic acid we have made only in sufficient quantity to assure ourselves that no qualitative differences are to be detected in the properties of the two acids, or in the habit of several of their salts.

Iodbromacrylic Acid.

Brompropiolic acid dissolves readily in concentrated hydriodic acid, (b. pt. 127°) and so rapid is the action that in a few moments the solution is filled with crystals of the addition-product. The crude acid is pressed between folds of filter paper, and recrystallized from hot water.

The acid separates from a hot concentrated solution as an oil, but at a lower temperature it crystallizes in pearly scales, which melt at 110°. The acid is readily soluble in alcohol, ether, or chloroform, but sparingly in benzol, carbonic disulphide, or ligroin.

I. 0.3800 grm. substance gave 0.1828 grm. Co_2 and 0.0307 grm. H_2O.

II. 0.2945 grm. substance gave 0.4480 grm. AgBr + AgI.

	Calculated for $C_3H_2BrIO_2$.	Found. I.	Found. II.
C	12.99	13.12	
H	0.70	0.90	
Br I	74.73		74.47

The solubility of the acid in cold water we determined by neutralizing the saturated aqueous solution, made according to the method of V. Meyer with baric carbonate, and evaporating with sulphuric acid.

I. 11.1382 grm. of a solution, saturated at 20°, gave 0.0785 grm. $BaSO_4$.

II. 10.8923 grm. of a solution, saturated at 20°, gave 0.0783 grm. $BaSO_4$.

According to these determinations, the aqueous solution of the acid saturated at 20° contained the following percentages: —

I.	II.
1.68	1.71

For the further characterization of the acid, we prepared the barium, calcium, and silver salts.

Baric Iodbromacrylate, $Ba(C_3HBrIO_2)_2.3H_2O$. The barium salt we made by saturating the aqueous solution of the acid with baric carbonate and concentrating on the water bath. From concentrated solutions it crystallizes in fine needles; from more dilute, in rectangular plates. The air-dried salt contains three molecules of water, which it loses *in vacuo* over sulphuric acid.

I. 0.4660 grm. of air-dried salt lost *in vacuo* over H_2SO_4 0.0360 grm. H_2O, and lost then nothing at 80°.

II. 0.2832 grm. of air-dried salt lost *in vacuo* over H_2SO_4 0.0208 grm. H_2O, and afterwards, when heated to 80°, 0.0011 grm.

	Calculated for $Ba(C_3HBrIO_2)_2.3H_2O$.	Found.	
		I.	II.
H_2O	7.27	7.73	7.35

0.4427 grm. of the dried salt gave, on ignition with H_2SO_4, 0.1498 grm. $BaSO_4$.

	Calculated for $Ba(C_3HBrIO_2)_2$.	Found.
Ba	19.88	19.90

The solubility of the salt in cold water we also determined.

I. 2.0636 grm. of a solution saturated at 20° gave, on evaporation with H_2SO_4, 0.0967 grm. $BaSO_4$.

II. 3.0991 grm. of a solution saturated at 20° gave 0.1457 grm. $BaSO_4$.

From these determinations it follows that the aqueous solution, saturated at 20°, contains the following percentages of the anhydrous salt: —

I.	II.
13.86	13.90

Calcic Iodbromacrylate, $Ca(C_8HBrIO_2)_2.3\frac{1}{2}H_2O$. The calcium salt resembles the barium salt closely in appearance, but is more soluble in water. The air-dried salt loses its crystal water completely *in vacuo* over sulphuric acid, or when heated to 80°.

I. 0.7622 grm. of the air-dried salt lost 0.0771 grm. H_2O at 80°.

II. 0.7172 grm. of the air-dried salt lost 0.0698 grm. H_2O at 80°.

	Calculated for $Ca(C_3HBrIO_2)_2.3\frac{1}{2}H_2O$.	Found.	
		I.	II.
H_2O	9.89	10.12	9.73

0.6518 grm. of the salt dried *in vacuo* gave, on ignition with H_2SO_4, 0.1465 grm. $CaSO_4$.

	Calculated for $Ca(C_3HBrIO_2)_2$.	Found.
Ca	6.76	6.61

Argentic Iodbromacrylate, AgC_3HBrIO_2. The silver salt was precipitated from an aqueous solution of the acid by the addition of argentic nitrate. It formed short, clustered needles, which could be recrystallized from water, with but little decomposition.

I. 0.4509 grm. of substance gave 0.1597 grm. AgCl and 0.0063 grm. metallic silver.

II. 0.7458 grm. substance gave, on precipitation with HBr, 0.3635 grm. AgBr.

	Calculated for AgC_3HBrIO_2.	Found.	
		I.	II.
Ag	28.13	28.05	27.99

With hydrochloric acid, the addition takes place much more slowly; still, after long standing, the chlorbromacrylic acid is formed.

Of the products formed by the addition of halogens to brompropiolic acid, we have thus far examined in detail only the tribromacrylic, although we have also made the diiodbromacrylic by the addition of iodine.

Tribromacrylic Acid.

Tribromacrylic acid may easily be made by adding slowly a slight excess of bromine to an aqueous solution of brompropiolic acid. The color of the bromine gradually disappears, and the product of the reaction separates partially in the form of an oil. This oil gradually solidifies, and more of the same product can be extracted with ether from the aqueous solution. The resulting solid must be well pressed out, and may then be recrystallized from chloroform, or, better, from benzol. Thus prepared, it forms colorless, oblique prisms, which are very soluble in ether or alcohol, less soluble in cold chloroform or benzol, readily in hot, and soluble in carbonic disulphide or ligroin. It is but sparingly soluble even in boiling water. Melting point, 118°.

I. 0.3449 grm. of the acid gave 0.1428 grm. CO_2 and 0.0183 grm. H_2O.

II. 0.1782 grm. substance gave 0.3229 grm. AgBr.

III. 0.1433 grm. substance gave 0.2625 grm. AgBr.

	Calculated for $C_3HBr_3O_2$.	Found.		
		I.	II.	III.
C	11.65	11.29		
H	0.32	0.59		
Br	77.67		77.13	77.94

The acid when boiled with an excess of baric hydrate is hardly affected, although it is slowly decomposed by a boiling alcoholic solution of potassic hydrate. We have as yet isolated no products of this decomposition.

The solubility of the acid in water at ordinary temperatures we have also determined by the method of V. Meyer.

I. 11.4429 grm. of a solution, saturated at 20°, gave, after neutralization with $BaCO_3$ and evaporation with H_2SO_4, 0.0597 grm. $BaSO_4$.

II. 12.7846 grm. of a solution, saturated at 20°, gave 0.0643 grm. $BaSO_4$.

According to these determinations, the aqueous solution of the acid saturated at 20° contains the following percentages: —

I.	II.
1.38	1.33

Baric Tribromacrylate, $BaC_3Br_3O_2.3H_2O$. The barium salt we made by neutralizing the acid with a solution of baric hydrate. On cooling the concentrated solution, it crystallizes in long needles, which effloresce over sulphuric acid.

I. 0.7888 grm. of the air-dried salt lost over H_2SO_4 0.0532 grm. H_2O.

II. 0.7585 grm. of the air-dried salt lost *in vacuo* over H_2SO_4 0.0506 grm. H_2O.

III. 0.4900 grm. of the air-dried salt lost at 80° 0.0324 grm. H_2O.

IV. 0.7024 grm. of the anhydrous salt gave, on ignition with H_2SO_4, 0.2185 grm. $BaSO_4$.

V. 0.4486 grm. of the anhydrous salt gave 0.1398 grm. $BaSO_4$.

	Calculated for $Ba(C_3Br_3O_2)_2.3H_2O$.	Found.		
		I.	II.	III.
H_2O	6.68	6.75	6.67	6.61

	Calculated for $Ba(C_3Br_3O_2)_2$.	Found.	
		IV.	V.
Ba	18.20	18.29	18.32

The solubility of this salt in cold water was determined by the method of V. Meyer.

I. 3.2130 grm. of a solution saturated at 20° left, on evaporation with H_2SO_4 and ignition, 0.2349 grm. $BaSO_4$.

II. 2.9600 grm. of a solution saturated at 20° gave 0.2170 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

I.	II.
23.62	23.69

Calcic Tribromacrylate $Ca(C_3Br_3O_2)_2.H_2O$. The calcium salt was made by warming the acid with water and calcic carbonate. It crystallized in needles which were permanent in the air, but lost in weight over sulphuric acid.

I. 0.4924 grm. of the air-dried salt lost at 80° 0.0099 grm. H_2O.
II. 0.8678 grm. of the air-dried salt lost at 80° 0.0248 grm. H_2O.
III. 0.4794 grm. of the anhydrous salt gave, on ignition with H_2SO_4, 0.1001 grm. $CaSO_4$.
IV. 0.8266 grm. of the anhydrous salt gave, on ignition with H_2SO_4, 0.1707 grm. $CaSO_4$.

	Calculated for $Ca(C_3Br_3O_2)_2.H_2O$.	Found. I.	Found. II.
H_2O	2.67	2.01	2.86

	Calculated for $Ca(C_3Br_3O_2)_2$.	Found. III.	Found. IV.
Ca	6.10	6.14	6.07

Argentic Tribromacrylate, $AgC_3Br_3O_2$. The silver salt is precipitated when argentic nitrate is added to an aqueous solution of the acid, but is more readily prepared from a solution of the acid in diluted alcohol. The salt is tolerably stable, and crystallizes in small, six-sided plates.

0.5267 grm. of the salt gave 0.1848 grm. AgCl.

	Calculated for $AgC_3Br_3O_2$.	Found.
Ag	25.96	26.40

Mr. Mabery has undertaken the study of the chlorbromacrylic and diiodbromacrylic acid, and will present the results of these investigations in a separate paper.

THEORETICAL CONSIDERATIONS.

Schmelz and Beilstein,[*] from a comparison of the formula of mellitic acid, $C_4H_2O_4$ (as it was then written), with that of mucobromic acid, $C_4H_2Br_2O_3$, were led to suspect a close connection between the two; but their investigations undertaken with the hope of proving this point yielded negative results.

In 1869, Limpricht[†] suggested that a series of compounds, among which were furfurol and its derivatives, contained a ring of four carbon atoms, and that they were therefore derived from an hypothetical hydrocarbon, —

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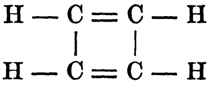
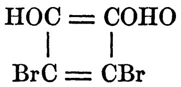
[*] Ann. Chem. u. Pharm., Suppl. iii. 280.
[†] Berichte der deutsch. chem. Gesellsch., ii. 212.



$$\begin{array}{c}H-C=C-H\\ \quad\;| \qquad |\\ H-C=C-H\end{array}$$

just as the various compounds of the aromatic series were derived from benzol. As the formula which naturally suggested itself for mucobromic acid he gives, —



$$\begin{array}{c}HOC=COHO\\ |\qquad |\\ BrC=CBr\end{array}$$

although I am at a loss to know precisely how this formula is to be interpreted. This hypothesis received temporary support from the discovery of the so-called tetraphenol by Limpricht and Rohde; * but further experiments made in Limpricht's laboratory failed to sustain it, and in the subsequent detailed account of these investigations † no allusion is made to it. In this paper Limpricht described the formation of fumaric acid by the action of bromine and water upon pyromucic acid, as well as the substance $C_4H_4O_3$, which he called fumaric acid aldehyde, and regarded as the product from which mucobromic acid was derived by substitution. In 1877 Baeyer ‡ showed that this latter substance was in fact the half-aldehyde of fumaric acid, in that it could be converted into fumaric acid by the action of argentic oxide. At the same time he pointed out the difficulty of supposing that mucobromic acid, which empirically was a substitution-product from this aldehyde, could be formed from it by the direct action of bromine.

In 1878, Wallach and Bischoff § published a paper upon the action of alkalies upon the β dichloracrylic acid, which Wallach ¶ had previously made by the reduction of chloralid. In a subsequent paper ‖ upon the same subject, they assumed that the structure of the dibromacrylic acid from mucobromic, which O. R. Jackson and I ** had shortly before described in a preliminary notice, was established quite surely by its ready conversion into malonic acid, and Wallach was therefore led to append a note containing a suggestion which he had previously made, that the constitution of mucobromic acid was probably represented by the formula, —

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* Berichte der deutsch. chem. Gesellsch., iii. 90.

† Ann. Chem. u. Pharm., clxv. 278.

‡ Berichte der deutsch. chem. Gesellsch., x. 1362.

§ Ibid., xi. 751.

¶ Ibid., viii. 1580.

‖ Ibid., xii. 57.

** Ibid., xi. 1671.

$$CBr_2 = CH - CO - COOH$$

In 1879, Toennies,[*] in investigating the action of bromine upon dibrompyromucic acid [†] in Baeyer's laboratory, found that a substance, $C_4H_2Br_2O_2$, was formed according to the equation, —

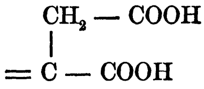
$$C_5H_2Br_2O_3 + Br_2 + H_2O = C_4H_2Br_2O_2 + CO_2 + 2HBr,$$

and that this could readily be converted into mucobromic by oxidation. This mode of formation led Toennies to the conclusion that mucobromic acid was the half-aldehyde of dibromfumaric acid. Further investigation in this direction Toennies relinquished in order to avoid interference with my work.

At the time of the publication of this paper by Toennies, my own experiments had shown that this view was in part correct. The conversion of mucobromic acid by the action of argentic oxide or other oxidizing agents into the dibrommaleic acid of Kekulé showed with sufficient precision that it was the half-aldehyde of this acid. On the other hand, it was evident that the dibrommaleic acid itself did not belong to the fumaric series, as could fairly be inferred from its mode of preparation; but that it was in reality a substituted maleic acid, since it could be carried unchanged through its anhydride.

A more direct proof of this fact was furnished by the discovery by Bandrowski [‡] of an isomeric acid of higher melting point, which could be converted into this by distillation.

Although it cannot be said that the constitution of fumaric and maleic acids is definitely established, the brilliant researches recently published from Fittig's laboratory leave but little doubt that the formula of maleic acid is, —



$$\begin{array}{l} \quad CH_2 - COOH \\ \quad\ | \\ = C - COOH \end{array}$$

If this view of its structure be adopted, the structure of mucobromic acid must be represented by one of the formulæ, —

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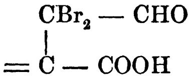
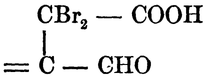
[*] Berichte der deutsch. chem. Gesellsch., xii. 1202.

[†] Ibid., xi. 1088.

[‡] Ibid., xii. 1232.



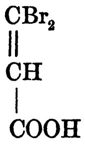
$$\begin{array}{l}\mathrm{CBr_2 - CHO}\\ |\\ =\mathrm{C - COOH}\end{array}$$



$$\begin{array}{l}\mathrm{CBr_2 - COOH}\\ |\\ =\mathrm{C - CHO}\end{array}$$

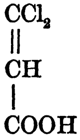
The ease with which it is decomposed, even in the cold, by alkalies and the aldehyde group thus converted into formic acid, would possibly incline one to adopt the first of these formulæ.

Unfortunately, no independent evidence concerning the position of the bromine atoms can as yet be drawn from the constitution of the dibromacrylic acid, which is formed at the same time, since none of its reactions give a clew to its structure. It may only be asserted, with tolerable certainty, that its formula is not, —



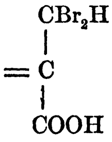
$$\begin{array}{l}\mathrm{CBr_2}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{COOH}\end{array}$$

since the corresponding chlorinated acid made from mucochloric acid appears to be essentially different from the dichloracrylic acid of Wallach, and the formation of the latter from chloralid shows its formula to be, —

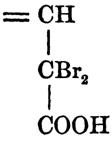


$$\begin{array}{l}\mathrm{CCl_2}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{COOH}\end{array}$$

If the structure of mucobromic acid is represented by one of the formulæ given above, it follows that the dibromacrylic acid obtained from it has one of the forms, —

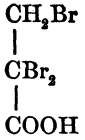


$$\begin{array}{l}\mathrm{CBr_2H}\\ |\\ =\mathrm{C}\\ |\\ \mathrm{COOH}\end{array}$$



$$\begin{array}{l}=\mathrm{CH}\\ |\\ \mathrm{CBr_2}\\ |\\ \mathrm{COOH}\end{array}$$

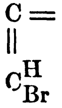
The formation of a tribrompropionic acid, melting at 116–117° by the addition of hydrobromic acid, would in itself be a sufficient reason for rejecting the second formula, if the structure of the tribrompropionic acid, melting at 92°, could be shown to be,—



$$\begin{array}{l} \mathrm{CH_2Br} \\ | \\ \mathrm{CBr_2} \\ | \\ \mathrm{COOH} \end{array}$$

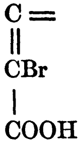
Although this is the constitution assigned to it by Michael and Norton,* it is evident that this formula is based upon a pure assumption concerning the structure of the *a* monobromacrylic acid from which it is made.

No more decisive arguments against the second formula can be drawn from the reactions or the derivatives of the dibromacrylic acid, although the formation of malonic acid follows more simply from the first formula, and the forms, —



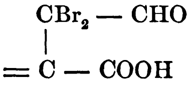
$$\begin{array}{l} \mathrm{C} = \\ \| \\ \mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{Br}} \end{array}$$

and



$$\begin{array}{l} \mathrm{C} = \\ \| \\ \mathrm{CBr} \\ | \\ \mathrm{COOH} \end{array}$$

which the second formula renders necessary for bromacetylen and brompropiolic acids, seem hardly in its favor. It would therefore seem probable that the structure of mucobromic acid is, —



$$\begin{array}{l} \quad\ \mathrm{CBr_2} - \mathrm{CHO} \\ \quad\ | \\ = \mathrm{C} - \mathrm{COOH} \end{array}$$

The close connection between the disubstituted acrylic acids derived from mucobromic and mucochloric acids and maleic acid makes their further study extremely desirable, more especially in order to obtain additional evidence bearing upon the position of the halogen atoms. Investigations in this direction are now in progress in this laboratory.

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* Amer. Chem. Journ., ii. 18.